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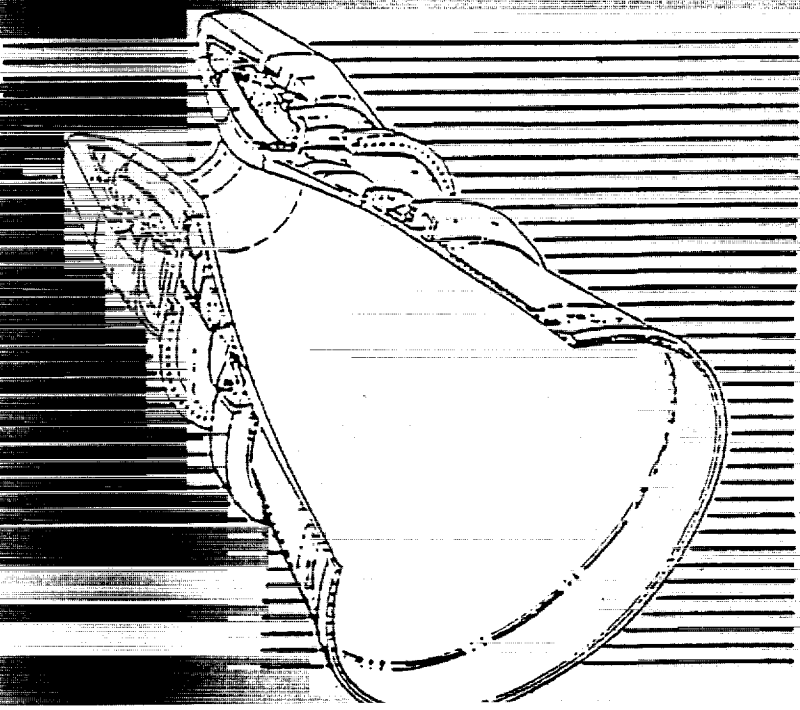
PROCEEDINGS
NOZZLE INITIATIVE INDUSTRY ADVISORY COMMITTEE ON STANDARDIZATION OF CARBON-PHENOLIC TEST METHODS AND SPECIFICATIONS

SACRAMENTO, CALIFORNIA
NOVEMBER 14-15, 1991

MARCH 31, 1992



MISSISSIPPI STATE UNIVERSITY

NASA GRANT NAG8-545

PROCEEDINGS
NOZZLE INITIATIVE INDUSTRY ADVISORY COMMITTEE ON STANDARDIZATION OF CARBON-PHENOLIC TEST METHODS AND SPECIFICATIONS

HELD AT

AEROJET
SACRAMENTO, CALIFORNIA
NOVEMBER 14-15. 1991

COMPILED BY

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PROCEEDINGS OF
NOZZLE INITIATIVE INDUSTRY ADVISORY COMMITTEE ON STANDARDIZATION OF CARBON-PHENOLIC TEST METHODS AND SPECIFICATIONS

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THE INDUSTRY ADVISORY COMMITTEE

FOR

CARBON - PHENOLIC CONSTITUENT TEST METHODOLOGY

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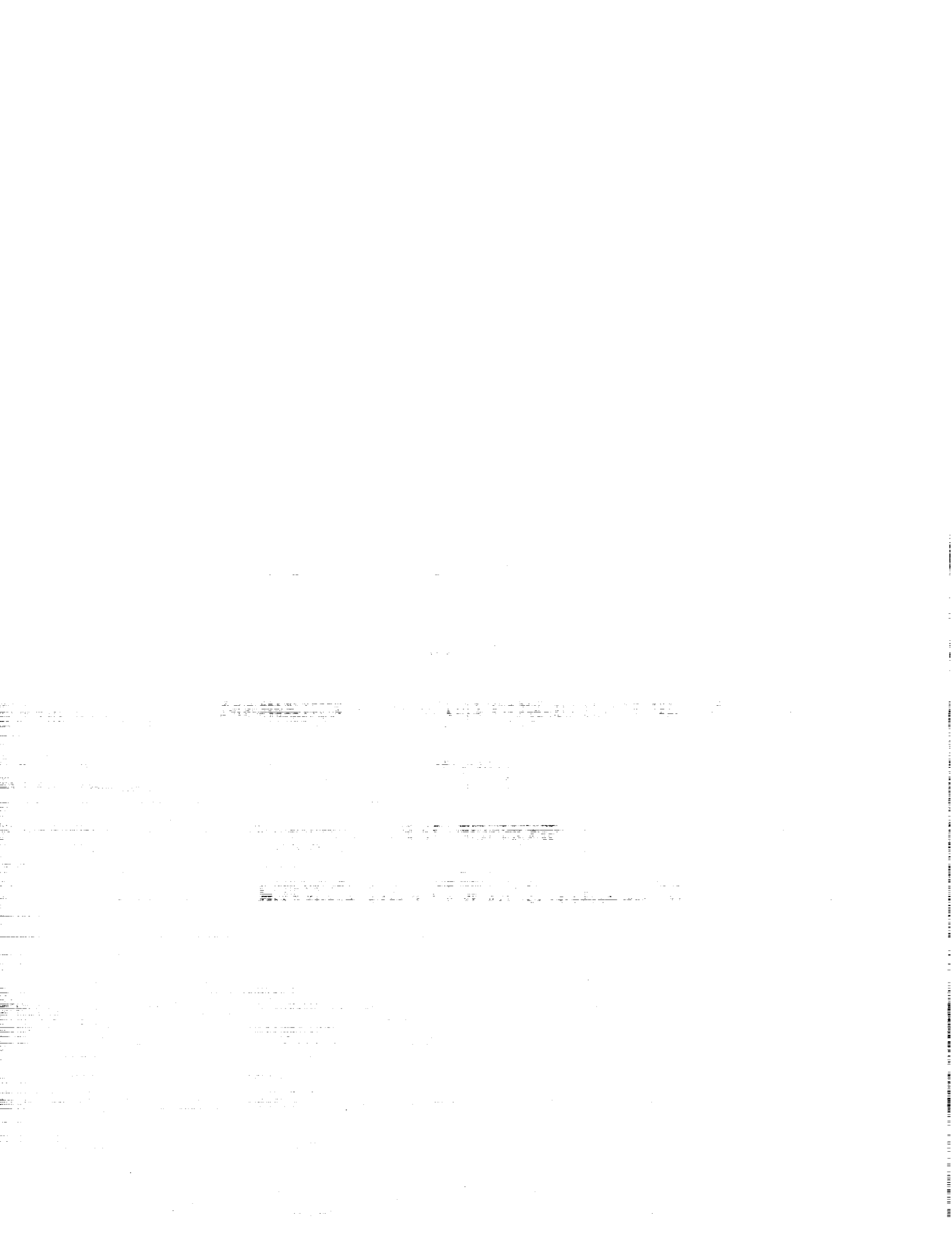

SPIP - NOZZLE INITIATIVE INDUSTRY ADVISORY COMMITTEE
ON STANDARDIZATION OF
CARBON-PHENOLIC TEST METHODS AND SPECIFICATIONS

AEROJET CORPORATION
SACRAMENTO, CALIFORNIA
NOVEMBER 14-15, 1991

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SPIP - NOZZLE INITIATIVE ADVISORY COMMITTEE ON CARBON-PHENOLIC CONSTITUENT AND COMPOSITE TEST METHODOLOGY

Gencorp-Aerojet
Propulsion Division
Sacramento, CA

AGENDA
Thursday, November 14, 1991

8:00 AM - 8:30 AM	Committe Preparation
8:30 AM - 8:45 AM	Welcome by Bob Harris, Vice President of Engineering, Gencorp-Aerojet Propulsion Division
8:45 AM - 9:00 AM	Introduction by Committee Chairman, Bill Hall, Mississippi State University
9:00 AM - 9:15 AM	Advisory Committee Progress Review - Pat Pinoli, LPARL
9:15 AM - 9:25 AM	Advisement Task 3, Resin Advancement NASA/MSFC New Technology Studies - Cindy Upton, NASA/MSFC
9:25 AM - 9:55 AM	NMR Studies - Cindy Upton, NASA/MSFC - Tony Day, Thiokol
9:55 AM - 10:55 AM	Solomat Instruments - Andy Matthieson, Solomat
10:55 AM - 11:15 AM	SPIP/PAN Development Summary - Keith Hill, Hercules
11:15 AM - 12:00 AM	Advisement Task 7, Product Code Identification - Pat Pinoli, LPARL - Ed Hemmelman, ICI/Fiberite - Ken DeVane, BP/Hitco - Jim Thomas, ICI/Fiberite
12:00 PM - 1:00 PM	Lunch

SPIP - NOZZLE INITIATIVE ADVISORY COMMITTEE ON CARBON-PHENOLIC CONSTITUENT AND COMPOSITE TEST METHODOLOGY

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AGENDA
Thursday, November 14, 1991

1:00 PM - 2:00 PM	Computer Modeling Support - Greg Crose, PDA
2:00 PM - 3:00 PM	Composite Testing - Eric Stokes, Sori
3:00 PM - 3:45 PM	Advisement Task 4, Carbon Assay Testing - Ken DeVane - BP/Hitco - George Peasley - BP/Hitco - Tom Paral - Polycarbon - Jim Suhoza - Aerojet
3:45 PM - 4:30 PM	Air Force Activity and Aerospace Computer Database - Ken Drake, Aerospace - Les Tepe, A.F. Phillips Lab.
4:30 PM - 5:00 PM	Advisement Task 8, Alternate Rayon Yarn Sizing - Tony Day, Thiokol - Bob Looney, NARC - Tom Paral, Polycarbon

AGENDA
Friday, November 15, 1991

8:30 AM - 9:30 AM	New Advisement Tasks - Fiber Morphology, RSRM - Carbon Microballons Specifications, ASRM - Tag End Specifications, ASRM
9:30 AM - 11:00 AM	Tour of Aerojet Facility
11:00 AM - 12:00 PM	Open Discussion of Issues Under Advisement and Assign Action Items

G. Brown — At this time I would like to introduce Bob Harris who is the Vice President of Research and Engineering here at Aerojet and I ask that he come over and say a few words of welcome. Bob, are you ready?

Harris — Welcome. This is quite a crowd. I would like to just say a few words about Aerojet this morning and just show you some pictures of some of our products. It turns out that most of what we make uses fibers and composites and most of you are probably used to what is going on in the solid rocket motor side, but even on the propulsion, we are getting into composite overwrap, tanks and we are actually making liquid rocket engines, chambers and nozzles with composites, so we have brought the liquid and solid companies together and have taken the technology developed by the solid rocket motor people and moved it over to liquid.

I want to show you a few view graphs about Aerojet and then some pictures of the products and then be on my way. How many people have ever heard of Gencorp? It is a household word here. Gencorp used to be General Tire. What happened was, there was a hostile takeover attempt several years ago and in order to survive, we borrowed a lot of money and we sold off companies to pay it off. We sold General Tire to Continental Tire of Europe, so now we are Gencorp, Gencorp-Aerojet. You can follow us on the stock market as Gencorp. The biggest segment of Gencorp is Aerojet and we do about $1 to $1.2 billion in any given year depending on the actual delivery of hardware. Gencorp Automotive does a couple of hundred million dollars a year and they are kind of on the down side, because they supply rubber sealing systems for the Explorer body. They supply plastic bodies for the General Motors A-Van. They supply Corvette bodies. Polymer makes commercial wallpaper and we make Penn tennis balls and racquets. Within Aerojet we have ordinates, 25-30 mm ammunition. Electronics system's biggest product line is the BSB satellite and that was used in the Desert Storm encounter. ASRM division, you are familiar with, is making the ASRM, obviously, for Marshall Space Flight Center. The Propulsion Division here in Sacramento is the combined liquid-solid company.

We were basically founded by Pierre Von Carmen in World War II to make jettison-to-take-off units to get heavy loaded aircraft off the runway. We were founded in Southern California in an orange factory with a few engineers trying to figure out what a rocket was. We have now moved all the rocket activity to Sacramento. We have 13,300 acres. That provides a buffer for primarily liquid rocket engine testing, solid rocket motor testing and solid rocket propulsion testing. We are in the process

of taking down about 200 buildings due to California regulations that are probably coming all over requiring labeling all things having to do with employee safety, like doors, fire extinguishers, smoke alarms. This will also benefit our customers in that we can take those buildings off our books and we won't have to pay taxes on them, maintain them, insure them. It is a way of streamlining the operation and decreasing the overhead dollars. We were $870 million in 1990 and in 1991 we will be about $1.2 billion and that will shift up and down depending on when things are shipped.

You came in right over here. This is the town of Folsom. This is Folsom Lake and this is the solid rocket motor facility. Liquid testing is here and we have acquired all of this area to provide a buffer for our test area. Our major concern is encroachment all around this side and this side where there is residential growth. We bought this property when it was in the middle of nowhere, now it is being surrounded and someday we will move, but that is 10-20 years downstream.

Here are some product pictures. You are probably familiar with a lot of these, Peacekeeper, Polaris, small ICBM. It looks like Peacekeeper will get one more by, by 9, which means we have to start working on by 10. Small ICBM, you can flip a coin on its future. Tacticals, we are involved in several Hawk, standard missile, Maverick and several new tactical missile programs we are now involved in. In SDI, we are taking this technology, and other technology that we have, into the ground based interceptor. Those are the two systems that are chartered for early deployment. From the composite-use standpoint, there are obviously going to be lower stages for these vehicles and the upper stage kill vehicle, we use a lot of composite overwrap, so we are taking all of this technology, moving it from the solid base to the liquid side.

Titan has been a workhorse for the Air Force. It delivers security payloads, classified payloads, Air Force payloads, NASA payloads, commercial payloads. It probably has a life of another 10-20 years. It will be phased out when the government puts the national launch system in place which will be a whole series of launch vehicles. That program is suffering like a lot of our programs. We feel happy this year if our programs only get stretched instead of cancelled. If the NLS is still alive and be funded next year, it is a hydrogen-oxygen core. It will have payload capability of about 20,000 pounds and the newer version will be 60,000

is still alive and be funded next year, it is a hydrogen-oxygen core. It will have payload capability of about 20,000 pounds and the newer version will be 60,000 pounds. When you put the ASRMs on it, you get that higher payload capability. We see the Titan as something that is going to be around for another 20 years, which is interesting when you think of all the technology, the solid, liquid, ICBMs of the late 50's and 60's. It is good technology, still working and being used. Delta is another workhorse. It has evolved in size and Michoud provides the 2nd stage propulsion on that. On the space shuttle, our role has been the OHMs engine. This is the only liquid propulsion engine that's gotten fully qualified for reusability, so right now we have project engineer and one program manager to provide spares.

We decided to get into the solids with the ASRM and this is being done at Iuka, Mississippi and one of the phenomena I think you can see in the propulsion business is they are becoming centers of excellence. MSFC is obviously going to be the liquid and solid center of excellence for technology and Marshall has a lot of people there. When we and Lockheed won the ASRM and we were going to do the enigneering here, we said we wanted a center of knowledge in Iuka and that is a euphemism for move all your engineers to Iuka. Now we are teamed with Rocketdyne and Pratt and Whitney on the STME, space transportation main engine, which will be used for the NLS and that engineering will be done here. I think the handwriting is on the wall that more and more engineering will be done at Huntsville.

We are involved in a national aerospace plan. Basically Pratt and Rocketdyne are providing the air breathing propulsion, but we are providing some components. We also have out in the back a high test facility. We have a 12 by 24 foot cabin. So we have a large new hypersonic wind tunnel capability now. We have started doing some of the work on the components that Pratt and Rocketdyne are developing.

Other new technology is get propellants. If the solids in the tactical world are being asked to become smarter, you either go to pivotals or ways to turn the solids on and off or throttle them where you go to liquids. A compromise is a gel. You gel the propellant so it loses a lot of its safety hazards. The thing we face in the solids industry is someday there is going to be a demand made to have no hydrochloride and perhaps have no particulates and so we see some movement, and also there is

going to be a demand made for clean ground testing and full life cycle handling of the propellant, the mixing process in the environment and the clean up process in the environment. Our entry in that is the A3L and basically it will give you the same performance so we are really enthusiastic about this becoming the propellant of the late 90s. It will find its way into space transportation and strategic offensive missiles, if there are any again, or if they elect to recreate a Minuteman, if the small ICBM falters.

Another interesting program that is kind of in the characterization of the single staged orbit from McDonnell Douglas, that is hydrogen-oxygen. When they looked at the propulsion, the rocket propulsion that was available and the efficiency that was available, they said we could probably make a mission on a single staged orbit. This program was started to try and demonstrate this. They call this the Delta Clipper and it is also the DCX. It is the next generation aircraft.

The ARS is just a typical tactical rocket we are working on right now.

The last thing I want to cover is resource recovery. What this basically is is a way to take solid rocket propellant and burn it in a fluidized bed incinerator and process fluids. As California goes, so goes the rest of the nation, so what we see happening here will probably go across the nation eventually. Open burning of solid rocket propellant will not be allowed. What this allows us to do is get the AP out in the precombusiton process and get the aluminum oxide out. Resource recovery, in the sense that we can sell the AP and the aluminum oxide and we can reduce the environmental impact.

Just to summarize, the Aerojet-Propulsion Division basically operating with strategic which is primarily solid rocket motors, tactical which is solid, gel, air breathing, space shuttle which is both liquid and solid, Titan and Delta, SDI, and hydpersonic vehicles and then satellites. That is what I wanted to cover today. I will answer any questions. How many people have heard of Gencorp?

Have a good meeting. It looks like you have a full agenda. Thanks for coming here and good luck.

Pinoli — Thank you, Bob. Bill, do you want to make a few opening statements?

Hall — This SPIP program is funded out of Marshall basically to improve our technology base. This committee is run by the executive committee that I would like to introduce so that everybody knows who to contact if you want to add something or have some comment that you would like to make.

We have Tony Day of Thiokol, Cindy Upton who is our technical coordinator from Marshall Space Flight Center, Pat Pinoli from Lockheed and Keith Hill, our representative from Hercules who is the prime contractor for SPIP. Any one of us would be interested if you have any comments. Does any of the executive committee have anything they would like to say?

Pinoli — This is the agenda. Tony are you prepared to bring up the rayon sizing issue earlier, rather than waiting for later in the day? Tom Paral is not going to be around tomorrow and I wanted to make sure that we get this activity presented. Let me go through a progress overview first.

What I had in mind for a progress review is to summarize the presentation made to JANNAF a few weeks ago. As Bill indicated, these are the committee participants and let's face it, without the support of the industry, this particular activity couldn't have made any progress. It has been a tremendous relief on my part to get the support from everybody here today. In summary, most of you know we have had seven prior meetings and the attendance seems to be at 28-30 per meeting and each one has been very fruitful. We started out with 5 tasks on the agenda and we have closed out three of them. We will be talking about some of these closed subjects today, because in reality you never completely walk away from these issues. Resin advancement will be addressed very hard today and it is an area that nobody feels very comfortable with old technology. Every one of the tests that we traditionally use has certain drawbacks and we keep looking for the four leaf clover or new technology that is going to bail us out. Cindy and Tony are going to be talking about using NMR to track the reaction. Carbon assay testing, we are in the throes of wrapping this subject up after we review some more data from BP Hitco regarding LECO equipment and calibration. The rayon spec issue is essentially closed out and we can't contribute much more at this time. Alkali metal content has been closed out

and we have recommended the RSRM burn off temperature of 600°C. Product identification code, I just wish you people would let me off the hook on this one. This is the bottomless pit. Maybe we can reach an understanding at this meeting and get this off our agenda. Rayon sizing; we are going to have a report of progress next on the agenda. Manufacturers and end users positions regarding code identification, the manufacturers are saying that the current codes that they employ provide adequate identification of the product. The information that the end users seem to want is in the certification data that comes along with that product. The argument therefore is if you want traceability; it is your job to take the cert data and somehow incorporate it into your data bank and maintain it. Don't ask the manufacturer to do your job. When you look at the product code, you really can't tell what you the product is what the end users would like, is changes in the product code which are traceable back with a product. If he had a simple industry wide code, he could hand that directly to the buyer and insure the product meets our need. The vendor could instantly determine what they need to meet those requirements. Another argument from the end users is that certification data does not follow the product to the end user. I know most certification data is generally lost somewhere in the end user system. These are the positions of both sides and I am open for any comments on the issue.

Beckley — Do you want to undertake this discussion now or when it is scheduled?

Pinoli — Let's pick it up later. On today's agenda is a study of rayon filament permeability. The permeability work is being done at SORI and Thiokol. The data suggests that there is something uniquely different about the NARC rayon, because the permeability of the hardware has dramatically shifted. Logic suggests that the mechanism whereby the residual volatiles get out of the composite is probably through the fiber itself. This permeability factor now has recently been significantly reduced. A request from the ASRM program is to address a new test methodology for carbon microballoons. Tag end specification, this is another ASRM program need. Some of the discussions that we had yesterday were along those lines. Thiokol has already taken steps to modify the current tag end mechanical property testing to improve the quality of acceptance data. ASRM cooperative tasks are electrical resistivity, moisture adsorption capacity, and a fiber density displacement fluid that is adequate for our needs. We also need a better residual volatile test. I

would like to move directly into the subject originally scheduled for 4:30 to 5, alternate rayon sizing, because Tom Paral may not be here tomorrow and being late on the agenda, we may not get to it today.

Looney

A little background for those of you who are not familiar with this, and if I misstate or overstate those of you who have involvement in this, please don't hesitate, please go ahead and correct me. What I want to do is elicit input from all of you because these are our thoughts of how the test should go and we may not have included everything that needs to be included. The objective is to eliminate the need for finish. There is only one reason for having a finish on the yarn and that is to give it friction protection. In our winding and twisting operation as the fiber producers and also at the weavers, it has to have some protection, some lubricity on the fiber to keep it from breaking filament. It does undergo a lot of fiber to fiber and fiber to metal friction. When it goes to the carbonizers they have no use for the finish. They don't like it and it does damage when it is left on. There has been a history of some residues left on causing weak fabric. The mechanism of that i will leave up to somebody else, because I am not the expert there certainly. The purpose of finding something that would add to the lubricity of the fiber, but yet be totally evolved in the carbonization, is what we are looking for. We would then, if we accomplish that, be able to reduce the chlorinated hydrocarbon emissions in the Los Angeles area, which is of great concern. We would also be able to eliminate a process step. If you carbonizers are not going to cut the cost, you better cut me off here. Mainly, we would eliminate the potential for weak fibers.

The approach involved, first of all, some laboratory sized quantities. Both Polycarbon and BP Hitco have the ability to do small quantities and do it in various ways. We would provide small laboratory quantities at three different finish levels and that could be done relatively easily at our facility in Tennessee and we could do this very soon. We did try one finish. Early on when we were being looked at as a replacement for AVTEX, some visitors to the plant asked for some samples of our products. We gave them samples of tire yarn, industrial yarn, as well as textile filament. They took one product and I heard this report. I have no idea of the validity of it, but allegedly, one of the products carbonized successfully without having to remove the finish. We tried that finish again. Logically you would think that would be the first thing to do. It didn't work. We sent some out to Polycarbon

this summer and Tom you can speak to that if you want. My understanding is that it was no different from, at least it did not pass. Is that right? Do you want to make any comments on that?

Paral — I have data we can look at in a little bit.

Looney — We would propose to put this on the low end, the middle and the high end. I can't conceive that we would want to explore much higher than what I have listed here because we don't anticipate needing to go higher than that. We are going to explore the extremes. We would also repeat for reproducibility. I wouldn't want to go into a large scale program without being sure we can repeat it. If that is successful, then we would have to make some fabric. Wayne this gets into your area, that we would probably want to provide you with enough to produce some fabric. I know at Highland you have to have 300 and something packages. We could provide that, but we would have to set up one entire spinning machine to produce this. We could do that, but of course that takes one machine out of production for a long enough time to produce these small quantities.

Testing would include these things. Perhaps not everything is listed that needs to be, but we would start off thermogravometric analysis and lubricity measurements and static electricity and broken filaments, windability. It has to work for the fiber producers and the weavers first. We are not going to provide something on downstream from us, but it wrecks our specification. We have to be sure Wayne and Tony can produce the fabric that is historically correct and we don't have too many broken filaments as a result of trying to give something to the carbonization process. We have veto power over this. If it doesn't work for us, it isn't going anywhere.

Ultimately, prepreg and fabrication performance has got to be included and I am not sure what all will be downstream from that. I would imagine that this can be qualified with some small motor firings and then say "Eureka, we have it" and go from there. That is up to somebody else.

Pinoli — We need to get this moving early enough through the ASRM program to be qualified as an alternate sizing. This really boils down to an environmental issue. You either accept a new sizing or you are not going to produce this in California.

Looney — I think ultimately, that if manned space flight programs, bless it, it will be blessed universally.

Mills — I don't think that is true by a long stretch of the imagination. If we can't get this product out of California, we may be forced to go with a 23X or whatever you want to call it. With enough lead time to get it qualified, we will have traceable results.

Towne — Is the issue solvent emissions or used solvent in California? It may be cheaper to move the operation out of California.

Paral — The problem is chlorinated solvents are on the hit list to be eliminated in 1997.

Day — Thiokol Corporation gave a presentation at Marshall three months ago, and by 1997 there aren't going to be any more of those in the United States. I strongly feel that what is going to occur is that EPA is going to limit the production of that. We are actively researching alternate solvents. They already have a timetable for when those things...

Towne — All chlorinated solvents?

Day — The ones that allegedly affect the ozone. The ones that we use are on that list.

Armour — ASRM is not using any chlorinated solvents.

Pinoli — Your points are well taken, but you are looking at this from the rational standpoint. What California is doing however is legislating out of existence your ability to purchase a chlorinated hydrocarbon solvents.

Mills — You are talking about 1997. There is already a requirement that you have to track all use of chlorinated solvent.

Beckley — We do that routinely. The plan right now is to use it wash off the sizing and then run a recovery. I know there is a degree of anxiety about the subject. My understanding now is the certainty that cleaner down the street will be closed down in 1997. There is another view that it won't be banned completely. The issue is a

little bit in doubt. Effectively, BP status is now that we are emitting less than the smallest dry cleaner is allowed to emit. Emissions now are below any minimum levels of the corner dry cleaning. We have hope of making one more improvement. If we get to the point where we can't buy it, then we'll have to make a change, but there is no eminent problems as far as the emission goes. If they literally stop making it because it can't be sold then we will all be somewhere with another finish. I think that we are certainly among the group amenable to evaluation of an alternate subject. I think we believe that it may not be as simple when you get into to meet all these criteria.

Drake — Is it possible that these rayon fabrics can be washed in one location and then shipped to the carbonizer? Maybe send it to the dry cleaner.

Mellburg — Along the line of what you are talking about here is that there is the need for an alternate finish. It is no longer debatable. It is given that there will be a finish. Optimum would be to produce 23 with no finish at all.

Looney — North American is just responding to a request. We are trying to come up with a finish. We have had two candidates in mind that we feel good about. Proof is in the doing.

Pinoli — I think there is another issue here beside the environmental issue. One could make a very strong case for all the problems that we have had in the past regarding the removal of the standard sizing that has been used for years by AVTEX and adopted at NARC. All of these products have had a detrimental effect if not removed prior to carbonization. That is enough justification for me to explore an alternate sizing.

Paral — As Bob stated, we did a little bit of preliminary work on carbonizable finish. This summer we got three different samples, two with an experimental carbonizable finish. This was actually the third and fourth attempt. The very first sample we got had a very low finish content of about 0.1% and that material did not have enough lubricity to it when we plied and twisted the material in our process. We had extreme amounts of filament breakage and could not even process through the subsequent operations. We terminated that particular trial without data being developed. The

second trial had about a 0.4% level. It generated some numbers even though it was weak. We wanted to take a look at two additional levels. These are the two levels that you see here.

This material was all processed through our system into 5 ply carbon yarn which is what we are using for the ASRM program. It is the typical 5 ply 1650 denier material. We ran 2 trial levels and one control. All of the material went through the same twister. Subsequently it was loaded on the same oven trays to low temperature and subsequently to that went through the same high temperature finish heat treatment. As you can see, basically the thing that we are looking for here, as Bob mentioned, if you do not remove the finish completely, the most obvious effect or result is the change in break strength. As you can see here this finish did affect break strength on this material. The normal control shows about average for our ASRM products that we produce.

Crose — Have you discussed the mechanics of this phenomena in the past and concluded that it is breaking strength and not damage to the filament itself.

Paral — We haven't really discussed that. I think Don has more experience in this than I.

Beckley — We have seen examples of stuck together finish, identified it microscopically.

Crose — What you are dealing with mostly is the mechanics of the cloth itself.

Beckley — Once you have this brittle material, then you are susceptible to filament breakage. You no longer have flexible material. You have damage occurring. An experience that we generally all had was just prior to the AVTEX shutdown. We were in a low breaking strength mode and that was always attributed towards the finish not coming off properly. Actually the data didn't demonstrate that it was much worse than normal. The difference is so subtle that probably, this is my pet theory, that many months of low breaking strength had to do with the yarn being wound up with a higher moisture content. The water content of that yarn can keep those filaments together so that they don't come apart in the carbonized yarn. A very subtle event. Myles' concern is echoed by us, but it is an area you can predict very accurately. The assessment that Tom has made is as accurate as we would have made.

Looney — I want to make it clear so that none you will go back and say that North American Rayon has a problem with its finish. This is a historic problem that we didn't invent. North American is trying to resolve it.

Paral — Remaining properties on this material seem relatively consistent with previous history. As evidenced here, the initial run through on these two samples did show a break strength problem. Bob's proposal now is to set up and run numerous trials. These take about 6-8 weeks to run through. If we can do numerous trials, we can evaluate several varieties at the same time.

Stokes — What is the control?

Paral — The control is standard finish material. This was one run. We had enough to make three skeins of material which is about 1200 yards each. The properties were so obviously degraded that we didn't do a lot of testing on this material.

Pinoli — Tony, do you have anything to add about potential materials that we might be trying?

Day — Right now, North American is working with their finish to generate alternatives. There really isn't a good way to predict how a finish is going to perform when carbonized on the yarn.

Towne — For years we processed high modulus rayon yarn without having to use a sizing. The thing that we did not address at that time was the disposal of the pyrolysis products.

Pinoli — Was that back before AVTEX production?

Towne — Back in the IRC days?

Pinoli — I got the distinct feeling that when AVTEX applied their permanent press finish to the product, the problem was greatly enhanced. I never got a handle on the sizings employed by IRC.

Myles has indicated that there may be cementation occurring. Cementation means different things to different people. I take cementation to mean that there is residue that bridges between filaments. You could also think of cementation as a fusion of filaments. Myles, your interpretation of cementation would be a bridging effect, or an actual fusing of filament.

Okay. Cindy, are you ready?

Upton

Before I talk about resin advancement, I want to talk about what those notebooks are. Last time that we met in Alpharetta I asked for your input because I had a big presentation to give on behalf of our group. The presentation went very well. In attendance were Robert Swinghammer, he's the Director for Space Transportation Systems. The chief engineer and program manager for both ASRM and RSRM and the SPIP managers were all there. They were very pleased with our results and our progress so far. In talking to the SPIP program managers this past week, basically what they are telling me is that I have to keep telling them so they can tell NASA headquarters what have we done for the solid rocket motor community. In their own words, "What have you done for me lately?" This notebook is a redirection of those charts from last summer. I included your comments that you gave me in writing. I had a lot of very specific NASA charts in there. I have taken all of that out. Some of the pages might seem a little NASA-slanted. Some of it I needed to update a little bit because there has been work done. I am hoping this can become a working document for us. Jim Suhoza was good enough to get this copied for us and put into a notebook. Each meeting we can add to that as we work on a task. We can just insert some leaves into the notebook and keep it going. I have found that once we got this presentation put together, that it was a very good living document. It kept changing. This gives you the charter in writing, a list of our current tasks and their statuses now. It has some details on each task listed separately. There are some pages describing our cooperative effort with other programs for the "what have we done for them lately" answer. That is what that is for. We have a few extra copies if you need them. Each meeting we will be giving you some extra pages to include.

What I am going to talk about today is resin advancement studies, what we have coming down the pike for our new work. We are going to be hitting resin advancement hard and primarily what we are going to talk about today is NMR.

Tony is going to talk about some work that he and I have overseen. The work was done by Dr. Tom Fisher of Mississippi State University. He could not be here today because he is giving a paper to the American Chemical Society. He has gotten some very exciting results in NMR. Some of the results are fairly preliminary, but we are both pretty excited about what we are seeing now. The NMR work is being funded primarily by SPIP, but ASRM and RSRM, are also contributing somewhat.

In the area of chromatography, from our discussion yesterday, I think that many of you have noticed that there is a lot of work that needs to be done. I will be contacting some of you and hopefully we can get a team together and we can start working on this. These are just some areas that I see would be interesting to look at.

Yesterday we toured Scott Brown's lab and he is already doing a lot of this type of work. Supercritical fluid chromatography is being done at Wasatch. We were hoping to send them some samples. We will be working on this in the coming months. Hopefully in the May meeting we will have some results to present about this topic.

We are also wanting to do some work with Gloria Ma and TEST, Inc. We have received a proposal from Gloria and we are trying to get some funding for that work. She is going to be doing some studies on resin filler content. We are hoping she can do some work on resin advancement, since she feels that this would be a good tie-in, particularly with the NMR. We haven't really done a lot of solid probe NMR work yet, so we really aren't ready to work with her yet. As I said last May, solid probe NMR is more difficult to do, but we are working on it.

Solomat is a very new instrument technique for our group. We have a representative here today from Solomat who will be giving us some results. It is not the person listed on the agenda. We have with here Rick McIntyre and he is going to give us the results of some of the work they have done. They haven't finished all of the work, yet. We have sent them some SC1008 resin and some cured resin. We also sent them 4 different prepregs and I think they have only had time to look at the MX4926. When those results are made available, I will be glad to pass them along. The TEST and Solomat work are funded differently. The TEST, Inc. work is funded

by SPIP and Solomat was funded by ASRM. The chromatography work is being funded by all these programs, SPIP, ASRM, and RSRM. The Foster Miller work will funded by ASRM. This is something I haven't started yet. I am just talking with the company. They had an article in NASA Tech Briefs that caught our eye. It is an FTIR cure monitoring procedure, but it is very new. Today we have some results to show you on NMR. We hope to be working on chromatography in the very near future and we have the representative from Solomat here. Tony Day is going to come up now and give us the results of the NMR work thus far.

Day

I have good news and bad news. The good news is that this will be the last time that I am aware of that you are going to get a lecture of a very advanced method of analysis by someone who doesn't know much about it. The bad news is the next time the guy who did the work is going to be here.

We are working on resin advancement with NMR, Carbon- 13 and proton NMR so far. As Cindy has indicated, we are going to try nitrogen-15 NMR when you get to that point because of the nitrogen component in there. We are sticking to SC1008 resin, primarily because we can get that. Occasionally in the past we have gotten some small specimens of 91LD, but that is covered by proprietary agreement, so we are sticking to SC1008.

The SC1008, this is an error here, it should say light. The first time I was aware of this, they did this on a 50 Mhz machine back in '64 and I got a copy of the spec on it in my notes. They did a great deal of analysis in proton NMR. Unfortunately, proton NMR of these types of materials are very complex and on a 60 Mhz machine, you just don't get the resolution that you do on a better machine.

I started doing what little I could do on the SC1008 back in 1987, primarily just to see what kind of information I could generate by that test method. I was really surprised at the detail that you could see. I was also surprised that none of that was in the literature anywhere. Currently the NMR on phenolic resins in undergoing something of a Renaissance. There is a group at Colorado State University and there is also a group in Canada that is working on phenolic resin. There have been some papers published. These date from about 1987-88. About this time period, somebody starting working on NMR on phenolic resins. One thing I will show you

today is that these spectra can quantify how complex the resin really is. We have always said and it has always been a historical fact that the resin is a very intractable problem. It is very difficult. At gel point there just isn't any information on what the density is, literally any information. We just moped along as well as could. We are going to attempt, by this technique because we have a solid probe availability, to look into that. This is not a quality control test, nor will it ever be.

I am going to show you the spectra and try to interpret them for you. I am not a nuclear magnetic resonance spectroscopist. We will go into the chemistry of the material and one of the conclusions that was a little bit of a surprise and that is that there are ortho and para cross links existing here. They can be between the molecules. They can be ortho, ortho or para, para or ortho,para, in those combinations. What we have found is that there are no ortho, ortho links in the neat resin which is a little bit of a surprise. This is not a quality control technique. So far this is still on neat resin as it comes from the manufacturer. There is data that exists that shows the cross linking, but I am not going to present that today, because we have just barely started in this program.

These machines are extremely expensive. The techniques are under going a renaissance. There are new techniques and some two-dimensional data that we generated that has not been available before. Also with the appearance of the high temperature superconductors, I expect that in the next 10 years or so, that NMR is going to go through another renaissance, because the equipment will change again. We thought we were on the cutting edge, and the cutting edge has moved. Eventually I hope we catch up to it.

I took an ACS short course on NMR at Virginia Polytechnic and while we were there we were presented with a rayon carbon fiber and they were able to get a spectra out of it which was amazing to me since I didn't think you could do that on that material. We had tried that at Thiokol Wasatch and generated pages of mush. They got a good signal out of it.

We have a contract with Dr. Fisher at Mississippi State University to do work on this resin as well as the work being done at Thiokol Huntsville. Hopefully next time they can present data.

Right now we are looking at the degree of advancement of the resin. We want to be able to get it into the prepreg and take a piece of prepreg and run a spectrum and find out where that material is. Ultimately, we would like to be able to take this method and use it for composite at any point in its life. I don't know if we are going to be able to do that.

This is a proton spectra. I have just written in some of the simple assignments. The big peak is the solvent, these two are related and then there is the solvent. The noise ratio on this machine, he is getting 2000/1 signal ratio. The good thing about it is that we run it at 300 Mhz which spreads these peaks out. At 60 Mhz it spreads these speaks out. These two little bumps here are the methylenes between aromatic compounds so that would be the hydrogens on the methylenes that are crosslinked. There is methylol which is the alcohol that is bonded to the ring and these are the aromatic hydrogens bonded. We haven't assigned much significance to the proton yet, because of this. This is a mess. There is really a lot of stuff in there and this is the aromatic hydrogen area. You see what kind of a detailed situation you have. Once again here are the two peaks on the hydrogen on the methylene. I have one that shows how you can make the assignments as to which one is which. I think that is the ortho one and that is the para one. The axis is in parts per million. This is a method so that you can tell frequency difference between peaks. Even though you get a little frequency drift between each run, you will always get the same PBM number on the bottom. It is characteristic for proton NMR.

This is a carbon-13 NMR. The others were proton NMR. They are looking at hydrogen nuclei. These are the carbon-13 NMRs. One thing to notice about this is the spectra width is a lot wider. It goes out to about 250 ppm. That is good. What is bad is that it is carbon-13 which means you have 1% of the natural abundance of carbon. You have this big range but you can't see much. It makes for good identification. This is not one of the better ones. What you can see in here now is that some of the assignments have been made. Once again you can see the isopropyl, but now this is a carbon on the isopropyl alcohol. This is the solvent that we used so there was no coupling between the carbon and the hydrogen. Here is the ortho, para carbon, methylene carbon and para, para methylene carbon and the predictive spot for ortho, ortho carbon is right underneath this solvent peak. I have always assumed there was always ortho, ortho linkages in there but they were under that.

We didn't see any. In advancing the resin they may show up and I will show you that in a minute. Here is the methylene bonded to an oxygen. Here is the carbon on the benzene ring. These two, this is a little bit of new information for me. These are the ortho and the para. This would be para. These are the positions that we expect to react in the course of advancing the resin. These are the remainder of the meta position and the positions that have adjacent carbons and down here, we have the carbons that are bonded directly to an oxygen in an o-ring. It is complex.

This is new information here because we did this in duterated chloroform moving the solvent peak from up here to down here. It is a predicted area, so the ortho, ortho linkages, there aren't any. That is not editorial. You can see it. This is basically the same spectra.

I believed since 1987 that beneath this acetone peak that there was another peak. That was one reason that we had them run it. We wanted to see that peak. Maybe it doesn't react as quickly, and it will come on later. I don't know.

This is a double piece of information. We sent Dr. Fisher two specimens, one of which was a specimen that Bob gave us back in 1987, L6J254, a real old resin. It was made in 1986 and Dr. Fisher took the two spectra and broke them into pieces and plotted them next to each other so we could see if there are any differences. I have kind of written my conclusions on here. Maybe not. There is a thing in carbon-13 NMR called the nuclear overhauser(?) effect and you can't really go, unless you know, unless I know more about how the spectra were generated, I can't really go making this kind of conclusion. I kinda wrote that down on the basis of what those looked like. At that level there doesn't seem to be any difference in the new resin and the old resin in the cross link.

In this particular area of the spectra I could see a little tiny bit there, but once again, maybe not. Basically what this little series of view foils show is that the really old resin, because it has been frozen, even though it has darkened on exposure to oxygen, compared to the new specimen that we got, on the spectra doesn't look any different. There is a slight difference in that piece and in the relative sizes of the resins. I couldn't see any real difference. The spectra needs to be cleaned up maybe a little bit. Here the carbon is bonded to the oxygen. Basically the as received new

one and the as received old one are very similar. The old resin had been frozen at 0° or less and it turns darker when you take it out. If you run a spectra on that darkened material you can't see any difference. It gets very viscous when you dry it out and there is no solvent left, but it is real dark.

Boudreau — If you run a test a the no solvent level, then the viscosity becomes a powerful tool for determining relative degree of advancement.

Day — In that respect, the data that Bob had shows that viscosity is a lot better of method of comparing resin than the GPC. You can see the viscosity change with small handling differences, but the GPC won't see that.

Beckley — Back in the Monsanto shutdown to Borden startup time, the resin was stored at 0, drum quantities and at 2 years plus, we passed through the viscosity window that we made acceptable. There is an aging phenomenon that is not picked up by NMR.

Day — I don't know what it is. Maybe if you keep it cold enough, you don't see it.

Beckley — This was resin stored at -10 in drums aged through the allowable viscosity range.

Boudreau — A brief comment on color changes. This is very characteristic of phenolic. The nature of the compounds are quinoid ones with air oxidation and I believe literally, parts per million, will give you the color changes and you are never going to find that in your NMR.

Day — That is right. The way to test for something like that would be chromatography technique.

New information that has been generated recently is from Dr. Fisher from tutti NMR and basically what you are going to see is a plot that looks something like this. What we have done is we have taken the signal from runs in two-dimension and the first thing you see is a HETCOR, which is a heteroatom correlation. Basically what we did was fit the carbon-13 spectra ran, took the proton spectra, ran it 90° to that and then through the appropriate software generate a plot that looks like this. In 3 dimensions the plot looks like this illustration, depending how deep you go down the

mountain. What you shows you is which nuclei reflected through a 45° plane are related to each other.

This is a HETCOR plot and this the region where the cross linking occurs. You can see this hill is correlated to that proton signal, so this carbon signal is bonded to or connected with this proton signal. These hydrogens here are bonded to those carbons. The same with these. What you see are these para, para connections, and ortho, para connections. Some of those are off down here, so it is not as simple as it appears.

There is another experiment called a double quantum filtered correlated spectroscopy. What you do with that one is these are with proton NMR spectra and what we are doing here is trying to relate which hydrogens are next to each other. It gives us more information on the hydrogen bonding or what is next to who in the structure. You need to see this initially, because we are going to look at this. There is a 45° plane of reflection through here and you can see that these are the same thing. There doesn't appear to be a lot of detail except down in here.

What you can see from here reflected through this 45° plane, take for example, I don't know which proton this is. If you line this up right, you can see this proton, reflected through this plane is connected to those two as well as, in a primary sense. In a secondary sense it is a little further away at these smaller ones. This is basically to show that the information has been generated. It has not been analyzed. You can see the detail that happens. What we are trying to do is see these here. What we are looking for is which peak along here is related to this peak along here.

In summary, in the as received material, no ortho, ortho methylene found. I will expect they will show up.

Boudreau — As you advance the resin, they will show up, but the fact that you could not find them in the neat resin is consistent with the known chemistry.

Day — Good. For me, I think BP people already knew this, but identification of the ortho and para phenolic carbon on reactive sites, we knew those were associated with the ring structure, but we couldn't unambiguously define them until we did those

HETCORs. The HETCOR link to the carbons, protons are still in analysis. The idea of saying this is to get this word out into the vocabulary. NMR has its own vocabulary that goes with it and they have tried to self-efface themselves as much as possible. That is where we are right now.

S. Brown — Tony, is someone working on the HETCOR analysis?

Day — Yes. Mississippi State is working on that.
Right now we need to be aware that this is not any kind of quality control test nor has it anything to do with any of the work that controls how you buy resin or use resin. We are just trying to find out what goes on with it. Until we can come up with a real clear picture, we can't tell anyone what to do about their resin.

Pinoli — Don, did you have something you wanted to say?

Beckley — As a continuing look following Tony and reflecting on what you do when you have an opportunity. That means you have people at BP research, you have NMR, and you have funding that has come available for the funding of research. We have been undergoing the aspect of trying to track the relative uniformity of our incoming resins with NMR, in particular, with the aim recognizing the same thing you have heard here. It is not a QC tool. It is an R&D tool. We have been trying to guide and direct it to the IR to make the two tie together. Today Dr. Roman Loza is working part of the cooperative and has brought us some of the information. This is not intended to be a complete treatise, but I think we are scratching at the surface.

Loza — My name is Roman Loza and as Don said, I work at BP Research which is the corporate research arm of British Petroleum here in the United States. We are located a little south of Cleveland. We are the former SOHIO, Standard Oil research facility. There are about 600-700 people on site and we have a large analytical department. We develop techniques for a wide variety of businesses. I just wanted to give you a short thumbnail sketch of what we have been doing for F&M on phenolic resin characterization.

There was some interest in finding out how much variability there is, from lot to lot, of both SC1008 and 91LD. What we have been doing is building a database using

C-13 NMR and FTIR. We have also carried out aging experiments (first at room temperature, then during prepregging) to find out how the composition of the phenolic resin changes with time.

Here is my idea of what the phenolic chemistry looks like. Anybody who is more familiar with this can interrupt me. The reactants are formaldehyde (in some polymeric form), phenol, and ammonia (or an ammonia byproduct), as the catalyst system. The first condensation reaction is the formation of methylols (there are a variety that can be formed from monosubstituted to disubstituted to trisubstituted). These then combine to give methylene bridges. I have just drawn two for illustration. Finally, during cure you have further polymerization (branching, ether linkage formation and methylene bridge formation to give a cross-linked product.

What we have done is similar to what Tony was talking about, looking at resonance in C-13 NMR. We have identified the following peaks. We then use integration to give a quantitative assessment of the resin. This whole area between 160 and 152 is the phenolic carbons (the CO). This gives you the total phenolic carbon content. We can identify the ortho-substituted and para-unsubstituted phenolic rings. There are formals in the resin as received. (methylene group between 2 oxygen atoms). This is a measure of residual formaldehyde. The formaldehyde is present as both an IPA formal and as a benzyl alcohol formal. Next are the methylols and there seems to also be an amine. Finally we have isopropanol. There is nothing extraordinary about the resins. One would expect all these compounds to be there, and they are.

Here is a typical NMR spectrum. We have been able to pick out this single peak as free phenol (unreacted phenol). Now we can quantify free phenol by integrating this small peak. We then calculate a ratio of unreacted to total phenol. This is a measure of advancement. As the resin advances, free phenol will react to form substituted phenol. The formals are here and also here. Methylols are here and here (obscured by IPA). We can integrate the IPA and then subtract out their contribution. The amine derivatives, we believe are here, and the methylene bridges are here. We haven't done any great searching for ortho-ortho linkages in the neat resin nor in prepreg. We are in the process of looking for them.

What happens if we store the material at room temperature for some finite period of time? We have monitored the extent of aging in the resins. We are trying to relate infrared and NMR to something that is easy to use, viscosity. We are trying to find correlations among the three. From NMR, we can get an idea of how molecular structures change. Infrared is something that is used currently and gives some information on structural changes. Finally viscosity is easily measured and, as I will show, can be used for determining how much the resin has aged.

We do our infrared tests in a slightly different way from the specification test is. We measure the infrared spectrum on the resin as received without evaporating the solvent. What we have found is that the most significant change in 30 days of aging is the disappearance of the 1024 peak. If you look at the NMR data, the only thing that is disappearing is free formaldehyde. We think the 1024 peak represents (there is some evidence in the literature) the formaldehyde formal, ether linkages. As formaldehyde reacts, the 1024 peak decreases. After 31 days it is essentially gone. If you purposely underconvert the resin, you see the same type of pattern. If you let solvent evaporate, this peak will also go away. By evaporating the solvent, you have thrown the system out of equilibrium; either the formaldehyde evaporates or it reacts. You lose resolution and don't see the 1024 peak. There is also a 828 peak. The 828/1000 ratio is one of the standard peak ratios used by F&M for QC. Free phenol has an absorption of 828, so its presence can affect this ratio. To use infrared more efficiently it is best keep the sample intact while you do measurements.

This is how the 1024 to 1000 peak ratio changes with time. We have taken this out to 90 days and essentially it is a flat line after here (30 days). This is room temperature in a closed container. Once the formaldehyde goes away, 1024/1000 peak ratio is fixed. It stops changing. How can we easily monitor the material aging as a function of time. We have shown an IR method, but there is something that, I think, is even easier to use; it is relative viscosity. The relative viscosity is the viscosity at aging time t divided by the viscosity of the same sample at time = 0 day. If you get a resin that is coming in at one viscosity at one time and a different viscosity at another time, you are going to get two apparently different aging rates (The slopes will be way different). If you ratio everything down to the viscosity at zero time, then you get a straight line. The correlation coefficient (r^2) is fairly high 0.986. It is a linear relationship out to 90 days. If you measure the viscosity of the

resin as it leaves the plant, and again before you use it, then you can use a graph like this to estimate the amount of storage aging the resin has seen. We have done this to several samples received from F&M.

This is material that nothing has been done to, we have not removed solvent. If you remove solvent, all bets are off. It has just been sitting there in a closed container.

Day — What you are saying is that any extra formaldehyde in there just gets used up?

Loza — Yes, it gets used up and that reaction stops and then another reaction takes over, but the continuum is to have viscosity increase at a uniform rate. This is resin as received that has been stored for some period of time. We are now in the process of doing this same type of analysis for prepreg, extracting the material off the prepreg and then analyzing it in the same way.

Here is what we do. We take the integration in the NMR and then we calculate which peaks have how much formaldehyde associated with them. At time equal to zero days aging, 11 mol % of total formaldehyde is present as free formaldehyde. As the resin ages this drops to zero. This is the genesis of the 1024/1000 peak ratio, going down, then staying constant.

Formation of the methylene bridges increases molecular weight. As methylols disappear, methylene bridges appear. The degree of substitution is also changing; however, it doesn't seem to change much. You are not really plugging up a lot of new sites. The degree of substitution changes much more slowly. What you are doing is using up unreacted (free) phenol.

Pinoli — Do you see any evidence of ammonia?

Loza — I think it is there. It is a structural part of the polymer. There are methylene groups next to nitrogen. We don't know exactly what those structures are. We just know where they appear in the NMR. This nitrogen derivative has been tentatively identified as an amine. The amount present remains constant during aging. From what we have seen it is the same in resin and in prepreg. The ammonia reacts first. It is an integral part of the polymer and it just goes along for the ride. It is basic,

so you are going to get some promotion for the reaction. I don't think it is a trisubstituted amine. It is probably a disubstituted amine.

Boudreau — You are talking about the other brand of resin, but...

Loza — Your resin doesn't look that much different.

Boudreau — The secondary amine should remain constant at this stage of the advancement. It won't be until you get temperatures in access of 150°C that those will change to double bonded nitrogen compounds.

Loza — We have not done any work on characterizing the nature of the amine species. There is a certain amount of it there and that amount stays constant. I think your resin is the same way.

Pinoli — One of the things I picked up on resole reaction is to use high strength ammonia for the initial step for the reaction or you could never induce the complete cross linking. Ammonia is a weak catalyst and full strength ammonium hydroxide is needed to get the reaction going.

Loza — This is basically what we have done to date. This is an impromptu talk. I wasn't really planning to give this talk until Don suggested it. What we are working on now is establishing a data base. We have analysis on 14 lots of 91LD and analysis of several lots of SC1008. We have established the baseline, so if we get a material that doesn't look good from other specs, we can now go back and say, "here's why it is different". We are working on prepreg extraction and analysis. F&M is providing material with different degrees of advancement so we can now look back and say what we are seeing is a continuum of reaction from the pot over to the prepreg and understanding what the reactions are. Using the quantitation of the NMR, we can get a good feel for how things are changing. Our work has focused on quantification. We have not been getting into the structural details as much. We are trying to be as quantitative about what we see.

Sutton — Can you correlate the viscosity with any of those measurements? It doesn't correlate with the disappearance of acetone, or degree of substitution?

Loza

It correlates with all of them, because all of those reactions are occurring simultaneously. It is not like one reaction stops and another one starts. It is a continuum of reactivity. Once formaldehyde is all gone, that is the fastest reaction. That, we can see where it stops. Whatever total structure you are getting, it doesn't have to be one structure that is causing that. It could be a multitude of structures, it just happens to be that it is linear with time.

Pinoli

Thank you Roman. Moving on to the next subject, Solomat Instruments, Rick McIntyre.

McIntyre

Some months ago, Cindy came to us with a request to do some analysis of resin. We are not specifically a testing house. We are an equipment manufacturer of an instrument for thermally stimulating current which is where you would typically apply a polarization field, to a material, specifically a polymer, quench the sample, freezing its re-orientation in place, reheat the sample and look at the movement of the dipole vis a vis current.

These are some types of information you can get. What we have done was take the cure process and set up a batch experiment. Typically our experiment process is one where we heat the sample up. We are using the neat 1008 resin and in another case we were using a prepreg. We heat the sample up to a region we would like to analyze, apply a field of up to 400 volts. Bring the sample down in temperature, take the field off and reheat. We would plot the results as current versus temperature. Current was being generated by the electrons moving. Initially, I had a phenolic resin that was in a pellet form that was supplied to us by people at Allied Bendix. They had a concern that there was a variation in the molecular weight in their raw material as it was coming in. What we found after running the sample, this peak at 130°, its location and intensity is indicative of material like this. There was a difference between 2877 and 3643. These numbers were given to us by Allied. To completely analyze the material is not our forte. One of the interesting notes was with this resin, this technique tested the material as is between to parallel plate electrodes as we ran the experiment. A small sample, usually about 1 centimeter square by about 3 mm high, placed between 2 electrode plates. Cooling is by liquid nitrogen and the system is evacuated so you can actually run drying experiments.

You can run aging experiments by elevating the temperature. Once experiments get started, they usually run in a field of helium as the heat transfer mechanism.

Now comes the fun an interesting parts, the neat part of the resin 1008. What you see here, we had to modify the experimental process a little bit. Instead of heating the sample up and bringing it back down, we have been able to program the instrument to run any of these stages. Essentially what we are looking at is the heating stage to dry the sample. These are all under no voltage, by the way. These are in degrees C. We took the sample from room temperature, heated it up 20° per minute to about 120° which was the prerunning temperature for the resin. You are looking at actual current that is generated by electrons moving. If nothing was happening, you would see a straight line, but we don't. The next step is not shown. We took the sample back down to 32° and then we ramped up at 25° per minute. We are looking at a decrease in conductivity. When the next batch starts up, there is a change in conductivity and mobility. The procedure is run again. This time from about 82-104°. We again see the general decrease which might be indicative of cross linking. This is the ramp to 104 which is actually the beginning of the cure time and then from here we go into the curve. This would be the actual cure duration of 60 minutes and then we ramped the sample up to 154°C for the final temperature. I have each of these as individual plots. This is the initial ramp. This is no voltage. This the ramp up to 104°. I understand this is the actual curing temperature of the material. These little anomalies that we see, I have no real description for. They are always there, even when we repeat the sample. Even when we did the ramp to 110°, initially, there are similar effects in the original ramps. There may be some reaction that we are scanning over and not stopping to actually see.

Ismail How do convert this current into a property of the material?

McIntyre In the case of a classical polymer, that current will be a function of the state of the polymer and vis a vis, its relaxation process. If there is more structure, there is less motion. Less motion will generate less current.

Pinoli — You are not really looking at the phenol formaldehyde reaction. You are just looking at an analog effect the reaction has on your equipment. The interpretation requires someone else's opinion.

Ismail — I'm having trouble trying to convert this current to some physical property of the material, like motion.

McIntyre — The principles of this technique have been in the literature since the 60s.

Beckley — Let me try to get to one thing that is bothering me. This is current flowing through the material and these are materials that have sometimes been used as electrical insulators, because they presumably don't conduct current.

McIntyre — This is the neat (uncured) resin. We are looking at the current generated by molecular motions during the curing process.

Beckley — Does the conductivity, because it is such a low current, flow relative, or is it due to the fact that you have 40% solvent in it and conducting through the alcohol?

McIntyre — I couldn't answer that.

Shaver — Do you have an applied voltage?

McIntyre — In this case we do not.

Shaver — I am an electrical engineer. How do you get a current?

McIntrye — When you heat the sample up, you are inducing the electrons to move.

Shaver — What causes it to flow in a given direction as opposed to random?

McIntyre — It is random. We are looking at the motion.

Beckley — Between the two plates you establish a voltage difference?

McIntyre In this particular application, you have an electrode which in this case is neutral, and the resin is actually liquid in a vessel. It sat on a plate. If this was a classical experiment, we would apply voltage to the material. In this case we are not. We are just heating the material up. Some of the anomalies could be the effect of the heat. The liquid actually moving. This one that I am pointing out here shows up at the exact same temperature range, in various ramps, in various samples.

Shaver Do you use different electrodes for different materials?

McIntyre We always use stainless steel.

Crose Do you read the voltage?

McIntyre In this case we didn't because these same electrodes are used to polarize the sample. There is a power supply to them.

One of the interesting things, following the cure schedule that was given us, Chuck, our technician decided to take it from the final temperature, ramp it back down, and then ramp it back up at 7° per minute ...

Ismail Are these currents going in opposite directions at the same time?

McIntyre Because of going down in temperature, in this aspect, and up in temperature in the other, we typically don't place a lot of significance on the directonality of the current other than to say there is motion. We are still looking at fundamentals. I don't want to try to interpret too much. Obviously there is an increase in motion around 87-90°. This is the same sample, we just accelerated the process. If we do this again, we may see this but to a lower degree this time.

Now comes the interesting part. That was the uncured, neat resin as given to us. Taking a prepreg, 4926, a little block of specimen, 2mm high by 2 mm square, running the same experiment. This was the result of ramping it up with no voltage to 110°, without a polarization field. There is a lot of processing that had been applied and a lot of materials had been added. There are differences. This again is rather interesting. The anomaly that fits in the general range of where we see those

other peaks between 85-90° range. An interesting point to me is the significant difference in appearance. This was taken from 32°C to 87°C where in the uncured, neat sample this went straight down like this. Here we see a general upward trend and it is rather noisy. The fact that there is carbon, carbon resin, carbon fibers and such, these are excellent noise producers. If you look now, there is a great deal less signal, as opposed to 10^{-9}. The reason for that low signal may be due in part to the material. It is also due in part to the ramping rate that we used. The slower the ramping rate, the lower the signal.

I didn't supply you with the complete experiment program.

Bhe — How was the sample heated?

McIntyre — These are heater coils wrapped around the whole mechanism. Instead of a vessel as with the next resin, you have parallel plates and the material is sandwiched in between the parallel plates.

Crose — Is it conductively heated?

McIntyre — Yes, in a field of helium.

Thomas — Was this prepreg cloth or prepreg resin?

Upton — I sent them the whole system. I sent them prepreg samples in dry ice.

McIntyre — I seem to remember talking to Chuck, and they were two or three ply samples.

Upton — They were thin. I know that they told us to keep it around 5 mm. It was some stuff that we had on the shelf.

McIntyre — Getting back to this. The reduced current flow could be a function of the heating rate. The spikes are most likely a result of the fibers in there have a great deal of carbon and the orientation of the fibers. We are looking through the fibers.

Beckley — In any of your samples did you induce a voltage?

McIntyre Some of them in the original test we did. The prepreg was extremely noisy. A lot of times in our documentation we ramp things at 7° per minute. That ramp rate corresponds to equivalent frequency for DMA, running at 10^{-3} hertz. The purpose for that is peak separation.

Again we see a little hop, skip and a jump. We have here a slightly higher temperature. We would have expected to see that around here somewhere, that glitch around 97°. Unfortunately, or fortunately, it is repeatable if you get another piece of sample.

Ismail Is this a fresh sample?

McIntyre We are talking about two samples. This is a new sample that is stage 3 of the process. We take the sample from beginning to end. These changes are not as great as 10^{-8}. Again you can have two processes going on here. Now you have filler, now you have fibers in here which can be inhibiting the motions.

In a slightly different venue, we decided to try to look at the isothermal hold. Because of the design of this model of the instrument, we couldn't hold the sample truly isothermal and read the current because it works in a time domain. What we did was ramp the sample for a total of 60 minutes to the 0.1° per minute ramp rate. In the course of an hour we elevated the sample 6 degrees. It is noisy and fairly uniform. I don't know the true significance. This is not current versus temperature. This is changing current versus time. This is the end of that isotherm. We have actually started now 6° higher up to 154°. It is difficult to place a lot of analysis on to the data that we have on hand because we don't have just one variable to consider going from the neat resin to the prepreg. A couple of points that I think should be made are that there was essentially no sample preparation that we made. We scooped the 1008 out of the vial, put in a crucible and stuck it in the instrument. The 4926 we placed between the two electrodes. We didn't look at the 1008 resin cured. That will be the next step.

Hill What fiber?

Day I think it was an AVTEX pre-shutdown.

McIntyre — I was told baseline material now used in solid rocket motor nozzle. This is what I had to go with on the analysis.

That is about it unless there is a specific question.

Ismail — What does TSC/RMA stand for?

McIntyre — TSC/RMA stands for Thermally Stimulated Current and Relaxation Map Analysis. The relaxation map is a separate segment of experiments, where you find a peak transition and break it down. Basically what we do, if there is a relaxation process going on, is try to break it down into its cooperative processes. We can generate Arrhenius maps for that will give a determination of the state of the glass. That is what the RMA stands for. It is an instrument originally designed to deal with polymers, and we have now dealt with molecular water, and all kinds of things now. We have dealt with phenolic resins.

Pinoli — Have we thought about sending him resins with degrees of cure?

Upton — That is our next step. We wanted to see how it work. We want to send some partially cured to see if they can track it and see how close we are. Right now we are just trying to learn how these different techniques can help us. We are looking at what is coming out in industry as well as updating present techniques. Thank you, Rick.

Pinoli — Okay, we are catching up to our agenda schedule quite well. Keith, do you want to go provide background and summary of the progress on the PAN development effort.

Hill — First of all, I have been really impressed with the meeting today and also today. Being a newcomer to this committee, I have been all ears. I have been associated with SPIP for roughly a year. Before that I was working on other programs with Hercules. Those of you who went to JANNAF and saw that nice video that FMI showed, Paul Martin, the firing of that nozzle, I was the project engineer on that motor at Hercules, so I was really thrilled to see that. I also worked as a project on engineer on the Pegasus, on the nozzle and I remember in early 89 when we were trying to define the design of the Pegasus nozzle, when suddenly someone dropped

a bombshell on us and said, "Hey, AVTEX is going out of business." I hadn't heard of NARC 23 yet. We were faced with what alternatives can we use and there were another PANs that were prospective. None of them seemed to be quite suitable because we were looking for an exit cone this thick. There goes your payload. I guess that was the impetus, when AVTEX shut down, for the PAN fiber development.

What I have been doing in the last few months, I have been involved with the 2-inch motor. I am not going to repeat the things that we went over at JANNAF, but maybe just hit a few high points and then just recently I have been asked in the last 30-60 days to come into the committee.

We have a test bed, this being the upstream and this being the downstream. We have these different positions for test materials. We have instrumented this thing heavily and tried to get a good comparison between the different materials. We did one test with some rayon material, the 5055B with AVTEX, and then we did one with complete NARC material.
The first thing we found out was that the test bed had some biases built into it and we had to analyze the biases in terms of position down the tube and neighborhood influences across the tube.

Pinoli — You split the ring into two sections, right?

Hill — Right. We can put a different material on this side versus this side and that introduces its own set of biases. I was kind of interested in one of the speeches Gary Wendell gave when he recommended that JANNAF go to a standard FPC or 40 pound charge test for evaluating material. You have standard dogbones, the reasoning was, why not have standard FPC. I think that is a very good recommendation. One drawback that we are facing here is that we are testing material in the environment. This throat right here is a 2-inch nominal diameter, 2.0, and these materials are 2.1 nominal diameter. The mach level is about 0.7 to start with. Of course, it varies as you go through the test. It is not a good place to test an exit cone material, particularly out in the aft end of the exit cone. The same with the FPC test that Gary is recommending. That would not be a good place to test an exit cone material, particularly a low density, low fired exit cone material.

Maybe we need to look at a test that would be suitable for that. We went through the list of materials that had been made up and that was based on expected performance and we normalized the performance of those materials to arrive at a ranking in terms of performance in that test bed. I have included here the FM 5055 AVTEX and also the 5055 NARC for comparison. We must keep in mind that this one had a different ply angle, a 45° ply versus everything else at 90° ply angle to the gas flow. The purpose was to show preference according to performance. It was also to identify the resins and fibers involved and what turns out is the P39 resin looks good. I must admit we didn't have a good test matrix or good enough experimental design to really ascertain for sure that one is better than the other. It was more or less a fruit salad of materials as I look at it. The Hi-Tech's 6K fiber was only fired at 1650, but it performed as well as the high fired fibers with the other systems. That was a surprise.

Crose — Has this been normalized for positional bias?

Hill — This is normalized for position as well as cross tubes, or as best as we can do at cross tubes. There is probably one more step we can do and that is normalize it actually with respect to neighborhood influence as well as positional bias. This does reinforce the notion for a standard test bed. Another surprise was with the 4921 with the SC1008. Then as you come on down in terms of erosion, you come on down to the NARC and about mid-pack here with that ply angle. How that would be with a 90° ply angle, I don't know. If it relates to the AVTEX, one could expect it would perform about like that.

One thing that would be useful, I guess going into this, everybody was concerned about what was the best material we can get. Now if held that workshop, the message coming loud and clear from industry, we don't care what is the best. We want something that we can use as a replacement in case NARC has a problem similar to AVTEX. What is a drop in replacement? That comparison, hopefully, if we had a good test bed, we could arrange that comparison in terms of erosion and have more confidence in it. I think that the confidence we have in this is merely that it does categorize groups of materials rather than discriminate closely between data such as 288 and 289 and maybe even 312 and 319. I think this test bed discriminates nearly that well. We just assume that it was group data.

When we look at the total heat affected depth information, again this is normalized, but only for positional bias in the axial sense of the test bed. What you see jumping out is the SC1008 resin seems to be doing quite well. Then you look a little closer and you don't have any one-on-one comparisons in this. One thing that does show up is that you would expect spun yarns to do very well in terms of total heat affected depth because of the lower char yield. That shows up. One would not expect to see high fired materials over here and they do show up down here. There is some credence to what we are doing. It does make some kind of sense in terms of group data.

When we began to look at this in terms of what materials we should recommend to carry forward into....

Pinoli — I know the intent was to keep the volume fractions all the same. Did you analyze the composites for volume fractions, fiber, and resins to see if performance was due to fiber loading content?

Hill — There is an effort right now. We have yet to feed that in and yet we are trying to feed that in with the density versus the normalized performance to see if there is some kind of a preference there. Ann Puckett is quite interested in getting this density data resolved to see if it doesn't sort out according to density.

We are going to move into a group of FPC tests, the same that Al Canfield reported on. We should have some pretty good comparisons coming out of that. Of course we will have 45° ply and 90° ply data on that. We are dropping some of the material from further testing. The ones we are dropping have to do with anything that has to do with a company like Heltra (?) that doesn't produce this spun fiber any more. We have two Heltra materials and we also have Hi-Tech's fiber not domestically available. When we actually went through and said if we looked at this and it is a requirement that we have domestic fiber, what does that leave us with. It essentially leaves us with Amoco, the T300s and the AS4 and Hercules. The others are all foreign sources of precursor. That narrows the selection down a tremendous amount. What we would like to do is take these positions and drop out and use lessons learned to make new materials. The type of things that we are looking at are, for instance, T300 fiber with the P39 resin. This shows the cross offs

in terms of the manufacturing, foreign versus domestic. We have only the Amoco and Hercules. BASF is also a domestic precursor. Those are only the low fired PANS. That is a different matrix than what we have worked here. None of these include the low fired PAN.

We have the T300 fiber we would like to put with the P39 resin. That appears to be a good combination. One thing that is a little bit distressing is that Hi-Tex's fiber 6K, fired at 1650, was our best performer in terms of erosion resistance and the PANEX also happens to be a foreign source and of the spun fibers that was our best performer in terms of erosion resistance. It may be what we are gearing towards is a replacement for rayon versus what is the best possible out there. We propose that we carry the Hi-Tech's on through the FPCs as a standard for what might be possible. We are also looking at the T300 with the P39 and other combinations having to do with AS4 and P39, so that we can get this matrix filled out. I don't know how many saw the firing down at Marshall the other day and in that particular nozzle we had some PAN materials in the exit cone. It was a three piece exit cone in the forward end, the NARC FM5055 and this is 5936 and 5879L. This material right here has been fired in a full scale Delta booster at Hercules. That was the same time this one was fired. We should have data coming in and that should show us the performance of PAN. When the data from these two come in, we will have a lot better update on what it is doing.

Cindy mentioned that we should be looking toward what we can do for the solid rocket motor industry. I suppose this is one thing we could do is provide materials such that if we have a rayon supply problem, there is something there to look at so the whole industry is not shut down. I believe there is a lot of potential with the PAN fibers based on the performance I have seen. There are still some real tough questions that have to be answered before they could be brought into a full scale program.

There is just one little closing comment I would like to make. When we talked about this committee, I understand this committee has to do with constituent materials only. Is that correct?

Pinoli We have expanded the charterto include tage end acceptance testing.

Hill — I can see a guy tape wrapping an exit cone and he gets a number that says resin flow and he doesn't know what to do with it. He performs his tack test with his thumb and then he adjusts the machine and we go from there.

Crose — There is something I don't think you brought out. Rayon has a tendency toward pocketing and PAN doesn't.

Hill — Let me show you this. In one test we had AVTEX rayon in all of these positions on one side of the blast tube and in this position right here, the 4th one back, we had the greatest amount of erosion. That is reflecting the positional bias we talked about. In this position we had the pocketing to a large extent. We didn't see that with the NARC product.

Crose — But the NARC ply angle was at 45° which should make it less likely to pocket.

Hill — That is right and the AVTEX was at 90°.

Beckley — The track record is that all rayon FPCs should have 90° and 45° sections. There is about a 50% rayon fallout. In the FPCs, surprisingly 3 out of x low temperature PANs are falling. That mechanism is really troublesome now. Rayon falling was attributed to low fiber tensile strength, but the PAN also fall.

Pinoli — I think we should make a point that the rayon based material that you evaluated in the test are RSRM grade materials. I don't think there have been any tests of the ASRM grade materials. These are different products. It would be erroneous to take the inference that rayon falls and PAN fibers do not fall. There is another generation of rayon based fiber coming down the road. The ASRM program is developing an improved product.

Crose — Do you feel you are driving toward a material that is less sensitive to spallation.

Pinoli — That is right.

Ismail — When you said that the Hi-Tech fiber gave you the least erosion compared to other materials, can you generalize that statement?

Hill — The general statement is if you have it high fired it will be a better erosion resistant material. You would expect lower erosion from the higher fired material. Over here we see the 2300° firing temperatures. These eroded less than the materials down here. This was the lowest eroded material.

Beckley — There is another data point which is 39 and T300 at a similar performance and it looks pretty much like something there at 1650°C.

Mellburg — Did Hitco provide you with those Hi-Tex at 1650 or was that post processed?

Hill — This is something I inherited. I went back to the annals of the SPIP and extracted this data.

Drake — Where did these temperatures come from?

Hill — Some say 1250+ and 1650+ and 1250 and 1650. I just took the highest in the group. I think they came from the suppliers. I would have to check for sure.

Drake — These could be best guess.

Ismail — They are not all correct firing temperatures.

Hill — What I would like to do is actually get these real temperatures out.

Pinoli — Thanks Keith. We have picked up an hour.

Regarding product identification codes we have finally gotten to it. Jim has a few statements to make. Beyond that I don't know if Don wants to make any further comments. I guess from the executive committee standpoint, we do have to come up with a consensus of how to respond back to NASA, what recommendations that we are going to be make and to have comfortable we are being constructive on this issue. I see both sides of this issue and I don't know what authority that we have to implement anything.

Upton — Pat, Mark Stucker told me last week that he considers this one our most important tasks to deal with now.

Thomas — Fiberite MX 4926 material can consist of the following suppliers: an AVTEX or NARC rayon yarn. The AVTEX yarn is pretty well identified for Shuttle program, D5, Peacekeeper. You can't use it anyplace else because the restart yarn was bought accordingly and it's gone through the system. Today's material will only be AVTEX rayon yarn. NARC is coming along and being qualified. The third firing is next week. There are no parts being built other than the test program parts and so forth. From a flight standpoint, maybe there is a part or two that is in anticipation of a successful firing next week. Within the woven area, we use both Highland and Milliken and Milliken right now is being qualified as a second source weaver along with the NARC rayon yarn, so it can't be used just yet either. Again we are back down to a sole source weaver. We do use three carbonized cloths, Polycarbon, Hitco, and Amoco. The Amoco is not going to be qualified with the NARC rayon yarn, so it will only be used right now for the AVTEX system. We only use Borden SC 1008 resin. I don't want to speak for Don and BP, but I can't believe that his system is much different than this right here. He uses a different resin, 91LD, but he has the same combinations that we have, because we all have the same program requirements. Everybody says they want a simplified numbering system. There is no simplified numbering system, is the way I see it. You can take 4926 and you can run through the sequence, AVTEX, Highland, Polycarbon; AVTEX, Highland, Hitco; go on down through the NARC material and so forth and all that does is identify the major suppliers that go into that system, but we don't put in anything from Borden. I didn't put anything in for resin, solid, etc. because you start bringing this list on out.

When you say you don't know what goes into the material, this is the first page of a cert sheet for Thiokol Space Operations. It identifies the 4926 broadgoods, date shipped, quantity shipped, Fiberite order number. There is a lot number. You come down here and you take this lot number and you trace it on through to the date of manufacture here. This is the mill spec that we meet, the Borden, Polycarbon. When you go to Polycarbon and you get their cert sheet, they will then go back to the woven white goods which will then pick up Wayne's lot number. Wayne will

then, when he provides his cert sheet, provide the appropriate rayon yarn lot number. This is just the first sheet of one for the space shuttle.

Pinoli — Jim, before we move from MX4926, if I were requesting the CSA data base, could I get that by going directly to the Fiberite lot number?

Thomas — We will have the Polycarbon lot number within our system.

Pinoli — But I have to go to ask Fiberite for the information?

Thomas — That's right. Just like Thiokol has the lot number in their system and they can tell you, not us, what nozzle that number went on. Then we will then take that lot number and we can take it back it to there, Polycarbon can take it back to Wayne, and Wayne can take it back to the rayon yarn precursor.

Pinoli — How close are you, Wayne, to being able to identify specific spools, if we wanted to trace rayon back to the lot of yarn.

Johnson — Specific spools? We just have the lot number, we didn't know the specific spool.

Pinoli — Okay. Just to clarify, what is a lot?

Looney — A lot is one truckload, same thing as AVTEX.

Drake — Does that signify a continuous run or anything like that?

Looney — Each roll has a sticker inside the cylinder of the cardboard tube that has a number that identifies where that lot was made, the history of the manufacture of that fabric.

Ismail — Yes, but when he weaves it and throws that tube away, it is lost, right?

Johnson — We don't do anything with it until it is ready to be committed to production. At that time we verify that their numbers are right. That has never been a problem historically on an individual, unless it is a broken filament or it is badly wound or something like that. The way that the yarn come out of any supplier, AVTEX or

NARC, you are not going to precipitately fall off the cliff. The historical precedence with AVTEX was that they would sort of drift downward, not out of spec necessarily. You might have to go back to them and tell them they were getting to close and get your act back together.

Pinoli — There is a certain degree of homogenization with the weaving process that diminishes the effect of individual spool variability. I was just curious about the traceability, obviously you'd have a stack of recorded spool numbers from here to the moon, if you were recording each spool location in the weaving process.

Thomas — This sheet happens to be for Kaiser. I didn't have handy a shuttle cert sheet, but this identifies the head end, tail end of the roll, the volatile content, the resin flow, and so forth. That all goes with this, again. Though the first sheet is missing on this one, but it would identify the Fiberite lot number here and you can tie it back to the yarn, the weaver, the resin system and so forth, and all that goes with each shipment of material.

Pinoli — But critical to all of this is the lot number.

Thomas — It always has been. The lot number has always been critical, Polycarbon's lot number and Hitco's lot number and weaving lot number and the lot number for the shipment of yarn.

Pinoli — Anytime you put a lot number on MX4926, that is your key to traceability.

Thomas — Yes. Whatever you want, you specify in your purchase order as to whether you want AVTEX or NARC or I will only accept carbonizer Z and if they are qualified, we will go let carbonizer Z do it.

Pinoli — What it tells me is that anytime you reference MX4926, a lot number should be included.

Thomas — If I take all of this and I look at going back through it and somebody says, well, I want a 1 number code, well, I could set up A, B, C through J and, there is just no way a single number or multiple letter or number will identify everything that I have

heard Ken Drake talk about, that I have heard Corky talk about, and so forth that says I want you to identify this with a single number. Also, once you make this change from either a 4926 or a 5055, you are going to change your traceability. In other words you are going to come up then with a new numbering system that you have to start all over and I think your traceability from your historical data base is going to significantly change on you. You are not going to be able to go back and run it through the system.

Last but not least, whatever change that is made to this, all of the users have to change their specifications. If NASA changes and pays Thiokol to do it and we have a 4926 or some number for the space shuttle and we have an old 4926 for the military, the military says I am not going to pay for it. Then you end up with the same material with two different numbering system. I think NASA has got to be careful as to what they think they want to do just to try to identify the material when it is contained on the cert sheets.

Mellburg — Jim, 4926 describes a generic product, but we make each pound to somebody's specification on a purchase order, so the part number that you flashed up there for Kaiser is a pretty specific product and has a specific pedigree.

Thomas — That is right.

Drake — Jim, you put another one up there with the material, can you put that back up? Can we get a copy of that?

Thomas — As far as I am concerned it is part of the presentation.

Pinoli — He is proposing that his code be employed.

Thomas — What I am saying is that if you want these through this what you have to look at, but once you take that away..

Drake — This code, did you create that?

Thomas — Yes. That is AVTEX, Highland, Polycarbon. These are the combinations.

Drake — Could these fibers also be low-fired or intermediate fired?

Thomas — It depends on these three companies, right here. The resin, filler, they are all variables according to what your purchase order requires, whatever you want to order.

Crose — Is the lot number unique with respect to makeup? In other words, would you never have a lot that consists of something from two different carbonizer?

Thomas — As an example, this lot number is 1122 pounds, and there will be another lot number for the next shipment that will be 560.

Drake — What fabric is this?

Thomas — This is 4926.

Crose — Is the lot divided to sell to several different customers?

Thomas — It can be. You can produce 3000 pounds and ship, it is all aerospace grade, unless you say I only want AVTEX yarn, I don't want NARC.

Crose — What are the ranges in size of the lots?

Thomas — Scott, can you help me on that?

Jackels — Roughly, the largest lot would be about 8500 pounds. A prepreg lot would a one-resin lot.

Crose — Does the carbonizer have trouble locking on to one of your lots?

Beckley — Yes. You have to when you have 8 or 20,000 pounds. The traceability is there to find out what it is and you know where it is, but there has been a lot of confusion about that one carbonizing lot and it would be impossible to make what shuttle wants, which is one lot of material-one nozzle. That is how they buy theirs. If you can

only use one carbonizing lot because it is not big enough from any one of the suppliers in terms of their definition of a lot.

Paral — For carbonized cloth, it's 2500 pounds.

Mills — That varies from program to program.

Paral — That is true. Some may be a thousand pounds, and 2500 for shuttle.

Mills — A question about AVTEX restart and pre-shutdown, were those given in lots of the prepreg?

Beckley — They were not at our place. There was a breakpoint, effectively, on a given lot and then it went to restart and if we were running it, they were separated. There was no one single prepreg lot...

Mills — You can go back and tell me that this lot is exactly what it was, pre-shutdown...

Thomas — It was pre- and post-shutdown.

Beckley — I am not really going to contradict anything that Jim said except to amplify that. The problem presented is when SORI wants to know what's in the laminate that they have and the traceability as far as we operate, the both of us, if they call you on the phone and ask what is this and they can get to that lot number, the information is available to anyone who has the need to know. I don't believe any legitimate problem has to be handled everyday with a 10, 12 or 15 digit number just to tell somebody what was in one particular roll of material. The traceability exists so that you can go back and put your finger on what that was, back as far as Wayne.

Boudreau — When someone is trying to trace a material, chances are they are wanting a lot of information and you are never going to get it all in one code.

Thomas — Everybody is going to want something different. Somebody is going to want to know which yarn, which rayon, which weaver, what was the resin content, what was the solids.

Boudreau — When you are talking about tracing, you are talking about so much information, that to put it in a code...

Mills — I have always been able to get to Fiberite and BP and get to what I wanted. I have got problems with 4926 being VCK, 5-harness satin, intermediate-fired, 4926 being 8-harness satin, low-fired, but it is still 4926 and the purchasing people have a lot of problems. They will go to Fiberite or BP and they are trying to buy cheap, and someone will say I can give you this 4926 for $60 a pound, or I can give you this 4926 for $120 a pound. Which one do you want? The purchasing guy doesn't know beans about low-fired, high-fired. I'd like to give him some sort of suffix MX4926A that tells him that I want some specific parameters. A good example right now is the low-density 4926 LDC. Right now I am not sure, other than the fact that I called and gave these specifications, that will tell them that I want VCK, because I am probably the only user of VCK, because it is more expensive, because that is what we qualified. That is the aspect that I am worried about. The traceability and getting information to SORI can be handled. It needs to be handled because a lot of the testing that they have done in that past, they have not had the information to tell me if the test data I have received is applicable to my material or whether I am making a mistake on whether I have high-fired and I need low-fired. It can make a difference in performance. It can make a difference in how you store it because of the moisture susceptibility of VCK, CSA, CCA3. There are things that you need to think about. I am not sure, I appreciate that some feel they are building themselves a nightmare, but I think that dismissing it and saying that we don't need it, well, I have given you some things to think about. Think about them and make your decision. If the decision is common across the industry, we will all have to incorporate it. If it is only going to be applied to the NASA material, I think that is a mistake.

Crose — Traceability can be handled by instituting a shared computer data base.

Mills — But that doesn't control the purchasing problem.

Thomas — The way you control your purchasing problem, you put on your purchase order what you want. If you want accept VCK, the specify what you want. That is all you have to do. There is not one single numbering product identification system that is going

to tell you, you, and you and everybody what they really want to know. One day they are going to say, "gee, I didn't know that was in there". Well, add another letter to the system. I just don't think you can do it.

Mills — My problem is that I get, "gee, I didn't know that was in there", about once a week.

Thomas — Then look at your cert sheet and it will tell you what is in there.

Mills — You are perfectly correct. The certs have been very good and it does give me a lot number and I pick up the phone and typically within a day, I have got the information.

Thomas — The only problem we are having right now with our traceability is with our older material that is on hard paper and our newer material is on computer and we are trying to get it all put on computer so we can recover it quicker. That is thing we ought to do.

Pinoli — You are doing that?

Thomas — Yes.

Drake — As we sat around the room this morning and I hear somebody talking about 4926. They have spent a lot of money to do an analysis or whatever, and they say what fiber is that. All of a sudden it is totally lost. Our design engineering used it much the same as he has. They are going to do an analysis and they say, "well 4926 is low-fired, or it has, they don't know anything that it has got, they just use the number that is in their data base and it is totally erroneous. They look at it as a part number, I guess. What I would suggest is a resolution to that. I look at product identification code. I think that is a misnomer. I would like to change it to recommendations for product identification code. I think it is really the hardware specification that should say when you have to re-identify it and how you have to re-identify. In this case, he has a spec for a material and if you change anything in your manufacturing, be it fiber, be it resin, be it filler, anything, then there is a change that warrants a new static firing. If so, okay.

Thomas — You think the product identification code is going to tell you all that?

Drake — No, no. I am not saying that. I am saying that you really need to control it to some specification.

Thomas — We do. This is a Thiokol spec right here. This is revision B, SCN 3 and 4 and if it's not for that, we can't change it.

Ismail — Does that tell you exactly kind of fabric he used?

Mills — It may or it may not. It depends on how specific you are in defining details in spec for qualified material. Navy specs for 4926 will not qualify CSA, CCA3, VCL, or VCK fiber. Air Force spec says the same thing. They have a list of qualified parts at the end of the specs, section 6, that says the following parts are qualified by whatever and it will list various combinations.

The other problem that I have is that I will have a vendor that has run out of material for his program. He has surplus material from another program he is going to transfer. He thinks it is 4926. He is not an engineer. He hasn't had access to this meeting. He doesn't know. It is a big problem and it is getting worse because we are encouraged to let the computers do everything and I don't know half the time when something is transferred.

Ismail — Jim, can you have like 4 specs in your computer, one for Air Force, one is for NASA, one for Navy, etc.

Thomas — This is a Thiokol spec for the shuttle and there is a Thiokol spec for D5.

Ismail — I don't see why you should have a problem, Ed.

Pinoli — The problem is they don't want to confuse a Navy qualified product with an Air Force qualified product.

Just a point of clarification. If the prepreg lot is being established by resin, then in that particular lot I could have an awful lot of different variations of fabric.

Wouldn't it be more appropriate to say I need the lot number and then the roll. Once you have that roll number, you can trace it all the way back to Tom's fabric.

Thomas — And that is just from this one sheet. There are probably 6 or 8 sheets that go into a certification package.

Pinoli — Each roll is identified?

Thomas — By roll number, yes.

Pinoli — So a combination of both those lot numbers and roll numbers will do it.

Thomas — Yes. Here are the roll numbers, 1A and 1B and so forth. the rolls are identified.

Pinoli — Put the roll number down and you have fabric traceability.

Thomas — Yes and this data comes out for each of the rolls. For the number of rolls that you have in there is the number of sheets you will have for the cert package.

Tepe — With the cert package, you always have access to the lot numbers. Do you store the lot numbers?

Thomas — We don't.

Beckley — The control document for up is made up in 6 copies for posterity. Accounting, QC, customer keeps a copy, ... Jim, if you want to go ahead, if not, I want to show you the approach we take.

We call this product identification code system, we call it a Grade Code, so you will hear me refer to it that way. What I have done is try to pull together how our system came to be, how we use it and we'll try to speak to some of the questions that have been posed.

This is a one page document and I will try to take you through it. First of all it is a Grade Code system for product identification and its primary purpose is to control

the product in house so that we can make the same material time after time. It is driven by resin systems and as you can see we have allocated the numbers between 200 and 299 to be a reference to elastomeric materials for this group the area of phenolics 500-599 is of particular interest and I have given you a couple of examples here. We have assigned the number F502 to SC1008, F508 to 91LD. Every principal resin of a given family gets a code number as long as we don't exceed a hundred of them, that will fit within that. If we have more resins in one system than that you can expand this with suffix letters. Basically, that has not happened to us.

The next thing that happens is that within that family and concentrate for a minute not on the phenolics which are generally speaking, a single component material. When you have an epoxy or polyester, you really need to define your resin as having a resin and a curing agent, in some cases a catalyst, so the way we function is we take a principal member of the system, which as an example would be E702 which would be a particular resin and then when we add additional ingredients to it, the curing agent and so on, they are added at a specific ratio. We call that a mix, resin mix, and that ratio is never allowed to change after it is established and that has a separate designation with the suffix letter. I gave you an example down here. 508T is taking 91LD, taking Carbospheres, taking elastomer, taking some other ingredients. They are all fixed in a precise weigh ratio and cannot be changed unless we change the T to another letter. Consequently from a change standpoint, the customer who is getting 508T can be assured that he is getting the same product. Now the way he does that is when we take the resin from here and add a reinforcement, we use a 4-digit code system, the numbers between 2000 and 2999. In this case it is between 5000 and 5999. That means to us that the resin system is frozen with an exact composition and in turn, the reinforcement is one reinforcement. That is a slight difference from the Fiberite approach. If we have to have a different reinforcement, we will do one of two things depending upon what the customer wants. We will take FM5055 with its legend of performance and the customer says he wants it with CSA, we will take a suffix and put it on the end of the designation 5055 CSA, because the product was not originally defined as CSA. If he wants VCK, which is the typical thing for Ed Mills, he gets 5055 VCK. We have also created a product called 5072 which also happens to be the same thing, 5072 is 5055 VCK. We will sell it either way. In either case there is absolute control, one reinforcement and one resin combination that goes with that product.

Drake — Don, does that include the filler?

Beckley — Yes, that includes the filler in an exact ratio. The example Pat gave this morning, an engineer calls up and says I want the 5055 and I want it at 6% filler, we honestly, respectfully decline to quote that product, because that is not the filler ratio that it is in. He can have what he wants. We will make him 6% filler in his prepreg but we will refuse to call it 5055 because the legend and the reference and the reputation is not built on that particular product. There are two ways you go. You go with the 3-digit system which is the resin. You put a slash mark and you write down the reinforcement, but that's not as easy as effectively having a 4-digit number that defines one product. That is our aspect of control.

We have a couple of things on here that you have heard about. 27, 28 and 29 are assigned numbers for qualified for fillers that are in that system and we have assigned USP numbers when we know we need to talk about that particle outside the confines of the 4-digit code. That is just a way of denoting it. This letter here, M, F, and T, happen to be the second digit of this series here, M meaning fabric, F is filament. I gave you an example of the FM for fabric, broadgoods. The FF is if you happen to be buying a roving product made with the phenolic resin. That would be an FF. The prefix before it tells you what the product is without knowing anything else about, you are there. The other 4 digits give you one specific product. It has to be one filament, a particular kind and one resin system that will only have one combination of ingredient ratios to the subject.

I think, pondering what we are going to do on the 91LD qualification transition, came from the site location and I'm projecting that if we put this digit in (X) in front of the FM until such time as the material has been concurred for qualification by customer and ourselves, then we will drop the (X). That will be on the materials produced with that new resin until such time that we can drop it away and ignore it thereafter. There will be an effectivity internally on when the resin switches over for production.

Pinoli — Can you have FM 5055 with any of those fillers?

Beckley — The answer to that is yes and if it is not specified, we use just 1. You can order it to the other two by specific identification, but they are qualified, that is qualified shuttle-wise and have been fired are available in case that filler goes out of production. I take that back. 27 is out of production. 28 is valid for today and we have qualified 29 as a backup.

Drake — If you are looking at 5055, you say you have VCK, pardon me, CCA3 fabric...

Beckley — That was the original designation of what 5055 is. It is one resin system and one fabric and one filler. As we have gone to subsequent fillers, we have actually given suffix designations to those. As we have gone from AVTEX to NARC, we have a suffix designation that is a change. That is 5055 and, I believe, for the product, as we change products, if the customer doesn't want it. In the case of shuttle, they refused to take the suffix letter for all the reasons of change and so on. For them, it will continue to be 5055B when NARC is implemented and they will have to do it with an effectivity time. This is now a discussion that goes with the program. In each case, the Navy will take a change. The Navy is taking their suffix designation change to switch from AVTEX to NARC. You have to work with each customer, and say "what fits your system?" One way doesn't fit all.

Pinoli — If we were to introduce NARC, the Navy would direct you to use B on the pr

Beckley — Right.

Pinoli — The other question I had, is if somebody wanted FM5055 with VCK; what do you buy VCK to? Myles tells me that VCK is a generic product. It is also produced to your specifications. What is your specification to Myles that you want the VCK manufactured to?

Beckley — The answer to that starts with the customer and what he is after and then we pass that back.

Pinoli — Okay, you pass issue to the customer, otherwise you are going to get a run-of-the-mill VCK.

Beckley We want to get a VCL. I am confident of that at this point. He understands our business well enough to know that is not the product we are ordering if we there was no other designation and at this point I think the rest of this group means 5 harness material, two-ply, 1100 and it means a firing temperature high enough to have moisture content and an assay that are...

Pinoli Is that right Myles?

Armour That's if engineers talk to engineers, but if we have purchasing people talking purchasing people that could go...

Beckley It could, but our purchasing department and their purchasing department have talked to each other for 20 years, so it hasn't occurred.

Drake Let's go back to the fillers for just a moment. You say that using the shuttle grade of filler was originally 5055B and it used USP 27.

Beckley Right.

Drake At some point in time, USP 27 went out of business and the customer directed you and you could use USP 28.

Beckley We qualified by firing 28 and 29.

Drake So now you are using the material with 28 as a standard as of an effective point in time.

Beckley Right. That is the way that it happened.

Drake It could be either one of them, because they are both qualified.

Beckley Well, the agreement with shuttle is that it will be 28 unless they tell us otherwise, or we tell them otherwise. The fundamental no-change clause overrides all of this. First of all, we don't change within the ratio of ingredients implied by any suffix letter on here without some reason that stems from a customer direction. Then the

suffix ties to a product designation over there, 5055J or 5055T or I think we are up to T now on 5055 and that will stay that way for that program and that specification unless there is come direction otherwise.

Drake — In the case of Ed, he uses the VCK. Do you call that also 5055?

Beckley — Actually, the way his procurement works out of CSD, they order 5072, which was the designation originally set up in our system to utilize VCK with the same resin system that is in 5055. Maybe a long way back, it all started with WCA, which was 5014, and the next customer wanted 5014 and its resin system, but he wanted it with carbon. For a while there, there was a designation 5014C-1 because he wanted to make the switch from WCA to a carbon material. At the same time we coined the number 5055 and that number stuck.

I cannot impress enough that for convenience sake and identification, you are all used to using those 4 digit identifications and the mind doesn't work very good on 5 and 6 digits. We have experienced it trying to see if that is the way to go and I will caution you, let's not go above 4-digits.

Pinoli — Don, could we make the statement (the same that we have made for Fiberite), that is if you designate the lot number, the roll number, along with product code, traceability is guaranteed?

Beckley — Absolutely.

Drake — So it appears that for data handling and interpretation, it is the simple solution to always specify the roll number, I mean to always specify the product identification and the lot number.

Mills — You don't have a problem with traceability. It is safe to say that is not a problem with either Fiberite or BP. If I have a lot number, I can get the information. The problem is the safety in ordering 5072 versus 5055 VCK. The safety there is that I don't have to have a purchasing guy that knows there are two different versions of 5055. I would like that kind of safety. I can give an example without looking to anyone in this room. The ATJ problem - my purchasing people bought unqualified

material and I went through a major exercise to show that it was really okay. They bought the wrong stuff, but it is really okay. But by the time you have got a motor sitting on the pad and you find this out, God help you.

Beckley — What was the origin of the chain? Was it originated at ATJ? He changed...

Mills — Yes, he changed and through an error in procurement, because we have a high turnover rate in procurement, we ordered material in 1990 and without knowing we got ATJ that different physical properties, but it was still called ATJ.

Drake — Let me ask Eric. He has done a lot of testing on these materials at SORI. Do you always have the lot number of the material that is in it and roll number?

Stokes — Our experience has been that the manufacturer has difficulty in locating the prepreg lot.

Mills — Are you referring to Kaiser, or the tape wrapper? When you say the manufacturer has difficulty locating the lot number, are you talking about me, the guy that sent you the material, or are you talking about the guy who did the tape wrapping or Fiberite or BP?

Stokes — I am talking about the fabricator.

Mills — We have never had any trouble going back through the carbonizers or the prepreggers.

Beckley — Our experience is that there is a purchase order between the prepregger and the fabricator, whoever it is, that ultimately lead to the identification of that material. Sooner or later, you can figure out which lot it could have been. Here it was made at this date, it couldn't have been laminated before that. It's not this lot, it's the other lot.

Mills — Generally it will have a number, you may get stonewalled, but you shouldn't. If you don't get stonewalled, you shouldn't have a problem.

Drake — Let me got back to Eric, once again. You are calculating A level design criterion on these that you are doing for NASA, CSD, and maybe some for Air Force. Do have lot numbers for all of those?

Stokes — My experience has been that if you get the lot number up front, then we don't have any problem. But some manufacturers and fabricators only hold those numbers for a year or so, and there may be a lag of three or four months before you get the material, and another 9-12 months before testing is completed, and by that time the records have gone into storage somewhere. Retrieving them at that point becomes difficult.

Beckley — I doubt if a 10-digit numbering system would solve that problem.

Stokes — For instance, we like to have the tag end volatile content, the resin content in our reports and you can't get that in a single number. You have to eventually go back to the lot number. Even with a 10-digit number, you are still going to have to have access to the manufacturing records.

Pinoli — I think identifying the pedigree of everything you are testing is getting more and more important for SORI. Without the pedigree, a lot of the data base we have now is highly suspect at this point. You have to know the vol content, the fabric and all the background before you can make a judgement. If you don't have that background, it is getting more and more difficult to interpret the test results from SORI.

I make a recommendation that we come back to this if we have time at the end of the session. I'd like to move on to Greg Crose, talking about computer modeling and what he is doing that might be of use to us in the future, Greg.

Crose — That previous discussion was a pretty good introduction to what I want to talk about, which is to somehow bring things together. I am involved in the Task 3.1 area of the SPIP program and I have been the one chosen to bring some of our thinking into your group and to take some of your thinking back to our group.

I think that more than anything else, this group is addressing the problem of reliability, or material variability. By all the things that you do, all the measurements you take, all the tests you do are oriented towards trying to make sure you understand and are alert to any possible changes in the products that we are using.

To get back to something from the previous discussion, I wanted to point out that from a design point of view, there is one carbon phenolic, FM5055, because it is the only carbon phenolic that we have a full database for when we do a structural analysis of a carbon phenolic part on a nozzle, it is either going to represent the database for the generic FM5055, or if we have a little bit of data, we are able to adjust our input so as to represent that material. For example, we may have a little extra data on MX4926 that will allow us to change our FM5055 model to better represent MX4926. All the other changes and differences that you talk about which aim toward uniformity of the product, doesn't get reflected in the design aspects from an analytical point of view. It gets reflected indirectly through designer's knowledge of a lot of the information that is generated by people like yourself. It is really no wonder that we have a difficult time predicting anomalous behavior ahead of time . If we test something once and it gives a certain behavior, we are frequently surprised when the 30th time it is tested it produces a different kind of behavior. There is no real connection between what we do on the analytical side and material variability information is generated by groups like this.

In Task 3.1, we are trying to apply the scientific method to understanding material behavior so that we can create data and computer programs to do a better analysis for design. Over a period of time in the SPIP program, we are evaluating data, building capability and then we are going to integrate this capability. We are starting out trying to understand more about the material from the scientific point of view, and converting that knowledge to engineering methodology for design.

One of the major outputs that we are looking for in this activity is to develop a computer code that a designer and an analyst can use to predict the performance of a given rocket nozzle and the materials within that nozzle. Another task that we have is to carry out an education that is basically a communication of all the things that we have found. In the science area, we are doing exploratory testing which allows

us to develop constitutive laws, failure criteria, governing equations. We are doing both experimental and analytical verification work. Everything that we are doing in Task 3.1 at this point is on the composite and not on the constituent parts of the composite or at various levels during the manufacturing process. It all has to do with the final cured component.

I'll just throw this out. Your group is talking about measurements of materials that are totally different from the kinds of measurements that we make on the composite and are used in our codes. The things that we use are stress-strain curves in compression and tension and the various directions within the material. We have to look at things like failure criteria. Then we have some analog testing that allows us to correlate our modelling of the stress-strain behavior and the free thermal strain. We do this at various rates because our properties are a function of heating rate. TMA, or thermal expansion is a function of heating rate and temperature. We do conductivity and one of the things that has been missing from our repertoire in the past is the modelling that is associated with the permeability of the material. Of course everybody always knew that the phenolic char gives up some of its mass in the form of a gas that flows through the pores of the material. That had never been explicitly treated within our computer programs and a big part of what we are trying to do in our analytical method now is to actually predict the internal pore pressures that are generally generated during that process which we think are related to important physical and anomalous events like pocketing or spallation, and ply-lift and perhaps a phenomenon they call wedge out.

Pinoli — How have you correlated your TMA data?

Crose — Well, we use free thermal expansion. That can be correlated to what you would create as TMA curves, but we use large composite specimens to do our measurements and we do it at various heating rates, various size specimens and various moisture contents to look at the dependence on those parameters. Our physical model of what is going on in an expansion test is that there is some expansion of the solid phase of the material, but most of the deformational changes are being driven by the materials response to internally generated pore pressure. What this really does is put the material, both the fibers and the matrix, into a state of tension and the expansion is a result of how stiff the material is in those two

directions. In the cross-ply direction, it is not very stiff and you get a lot of deformation and in the with-ply direction, the fibers are reinforcing and they don't deform much, but they load up. When we do a composite analysis that does not involve the generation of pore pressure explicitly, then that whole behavior is mixed into the properties that we use to do an analysis. We need to be very careful about how we interpret the results of that kind of analysis. On the other hand if we can explicitly treat the pressure generation, then we have another problem which is to take the pressure generation effect out of all this data and then do an analysis that way. Then we have more meaningful results.

Pinoli — I have heard you are going after gas permeability in about three different ways. I am curious as to which portion of that data you are using in your model.

Crose — We have some research work going on, and this shows some of the results of using a new one-dimensional code that has been created to couple the generation of pyrolysis gases, flow, and development of internal pore pressure with the deformational state of the material. This code has been correlated with free thermal expansion tests and it has been correlated with the restrained thermal growth (RTG) test, which are two extremes of material behavior. also we are applying it to the RSRM exit cone and this is the first time that we have taken permeability data, measured at Southern Research, and put it into a code that can use it in an intelligent fashion where the gas flow and structural deofrmations are coupled. This code also has the capability of predicting temperatures, but we did not use that feature. The input temperature distribution is shown on the viewgraph. As a result of this temperature distribution which we can also correlate to a degree of char, the code can calculate a pore pressure distribution which is this solid line. Through most of the char layer there is very little pressure buildup. Pressure builds up to a level of about 2000 psi within the material which is at a temperature of around 500°F or a little cooler than that. In the case of the exit cone, the cross-ply tension stress is almost totally in equilibrium with the pore pressure buildup so the cross ply tension stresses look something like this. If you compare the stresses to the strength of the material which is temperature dependent, you can see the code is predicting that there is a region in the material where the predicted stress is a little larger than the strength of the material. Basically what we are doing is saying, is that in this zone we should have ply-lift, but it doesn't ply-lift all the time. Those are some of the variabilities

that I would like to talk about it, but on a nominal sort of basis, the code shows you are on the threshold of that undesirable kind of performance. I would say that this is the first time that we have ever taken data and used it an analysis without tweaking any knobs, and came close to predicting the ply-lift phenomenon.

We don't think we have all the physics in this code that we need. Some of the physics that are missing are the two-phase behavior of steam and water and what we have here is a permeability and viscosity that is associated with steam in a model, but in reality there would be water condensation and a higher viscosity of the water, so there would be less of a pressure build-up. This pressure probably peaks more in the hotter region and doesn't permeate so far into the cold region. In order to get to that prediction, we are going to have to treat it as a two phase system. When we do the analysis without treating pore pressure explicitly, then you can get compression instead of tension since this whole response is being driven by the pore pressure,

Pinoli You are convinced that pore pressure is the leading cause for ply-lift.

Crose I am totally convinced that pore pressures produce ply lift.

Pinoli Do you feel that it is the only thing that is the contributing factor.

Crose I think that you can change the tendency to ply-lift by design. I think you can change the tendency by the way the material is made. If you change the ply angle you can get a different response out of the code.

This chart shows permeability versus extent of pyrolysis, and more than anything else, it is what we need to this kind of analysis. It is the code input that we use to get results and is constructed using data from Southern Research Institute (SORI). The data from SORI is permeability versus temperature and stress level on a specimen. What we have done is convert that to permeability versus extent of pyrolysis and strain level (cross-ply strain level). The actual tests were done at various temperatures and various cross-ply load levels on the specimen and what they found was that permeability would kick up rather dramatically with temperature, like 700-800°F and it would kick up at different temperatures depending on the load level. Basically this indicates that as the material is compressed, the permeability

goes lower and as the material expands the permeability goes higher. The permeability at elevated temperature out in the char layer is very high. When the permeability is low, it is very difficult for the gases to get out. You can relieve pore pressure by expanding the material. This is like a free thermal strain test. When you are down in these strain levels, this is like a RTG test. Also, what we have noticed in the material which is really alarming to me, is that there is a variation in room temperature permeability from this level which is what SORI calls nominal, down to 10^{-18} which is some of the current material.

Day — Actually the lowest permeability that we have measured on this carbon phenolic is about the same as nylon or mylar.

Crose — Okay. This is extremely interesting to us because...Well, I will show you the next chart. I did some sensitivity studies where I brought the room temperature permeabilities down three decades. The reason I carried it back into the other data is because there is no evidence that the permeability is different at the higher temperature. All we know is that the permeability is quite variable at room temperature.

Pinoli — You really have no high temperature data that you can hang your hat on.

Crose — I think we do. Eric Stokes thinks so. This is all Eric's work. He might want to make some comments. The other thing that is really interesting is that the room temperature permeability according to Eric is probably controlled by flow of gases through the closed crenulation channels of the fibers. What is disturbing to me is that high temperature permeability may be pretty much unrelated to this low temperature permeability. In fact, it undoubtedly is. When I went through and I connected room temperature permeability to elevated temperature permeability, it was taken to be a smooth curve. I may be missing some of the physics. Up in this temperature range, you have to get gases out of the matrix and then out of the material. How do the gases in the matrix get into the fibers to get out of the material? Or do they get into a porous microstructure that is created as part of the pyrolysis? There is a lot of complex behavior associated with this phenomenon.

Pinoli — We are talking about activated carbon now, and we are moving gases into that activated carbon pore structure The question is, if we have condensable gases going into the pore structure, all kinds of things could happen.

Ismail — Up to now I have not known the difference between the permeability he is defining and pore structure. i think you are talking about two different things here, Pat. I don't really understand what he means by permeability of gases. Is it from one layer to the other or is it....

Pinoli — You should go to Eric and have him explain how he is measuring permeability.

Stokes — Permeability is the ability of a material to allow gases to flow through in repsonse to a pressure gradient.

Pinoli — You have activated carbon. As the water tries to get out of the composite, it is going to flow into that micropore structure and ultimately it will be channeled through that pore structure out the fiber.

Ismail — Not necessarily, Pat. It might be going around the pore from outside. You are assuming that the micropore is open from both sides and here we have some...

Pinoli — In his composite microstructure, he sees no microcracking or separation between the matrix fiber interface; therefore, the only mechanism he can justifiably say for the transport, is through the filament itself.

Crose — When I did my model, I had to connect something happening down here. When you run a code, you have to input all the variables whether data or not. One of the things to think about is that some of the phenomena that we are struggling with in Task 3.1 and some of the work that you are doing with the material at various levels in the process can offer insights into this are.

Beckley — I am really disturbed about the 400-500° temperature range, indicating that there is pore pressure. I have a feeling that if we put a balloon over the material at 400-500°, we would never find any significant gas generated. At the same time the

thermal expansion coefficient has shown a large cross-ply growth which is, if I understand, is thermal expansion.

Crose — You don't have to have a flow to have pore pressure.

Beckley — If you don't have to have a flow. What is it?

Crose — The material will accommodate a given level of pore pressure either by expanding which lowers the pressure or it will build up pore pressure because the material is not able to expand. As far as that phenomena being expansion, there is no good physical explanation of the solid phase being heating rate dependent. Expansion comes about from how much the atoms vibrate and so on and there is no time lag for that kind of phenomena. When we do expansion tests at slow rates, we don't get enough expansion to develop the kind of stresses that we are worried about. We are only getting that expansion at high heating rate. We attribute it to the diffusion properties of materials. The expansion at the 300-500° range has almost got to be due to water (whether gaseous or liquid).

Ismail — What size of pore are you defining here?

Crose — Pore size? It is not a part of our analysis.

Ismail — It doesn't matter what shape it is?

Crose — Oh, it matters because that will influence the permeability data which goes into our analysis. The other thing that goes into the analysis is when you have mass loss and deformation, we assume that you develop porosity which becomes a storeroom for the gases. The gases can expand into that porosity, but we do that on a volumetric basis. We don't address the size or shape of a given pore. It could be a million little tiny ones or one great big one. It doesn't matter, from a model's point of view. We don't have any information about what pore size distribution might be. If we did, we might find some way of answering these questions.

Okay. Let me go on here. I may have to start skipping some things. In Task 3.1, these are some of our goals. With analysis codes, we want to predict the average

response and the standard deviation of that response and we want to achieve confidence in our predictions. In terms of failure criteria, we also want to predict average and standard deviation and again achieve confidence. In the application of the technology, we want to verify the predicted response and verify calculated margins. This would be a Task 3.3 kind of activity. Predicting the average response, predicting the average strength is a 3.1 activity and looking at material variability and confidence is a joint 3.1, 3.2 activity, the way I see it. Let's look at our goal this way also. If you look at what we (Task 3.1) are trying to do, this represents an ideal. If we have the perfect analysis code and the perfect data input and the perfect information about failure criteria, we could draw curves that look like this. This curve would represent the response of the material in terms of some quantity that describes a failure event. This would be a different quantity for every failure mode. For example, for pocketing, this might be fiber strength. Look at the relative probability of occurrence. If your material has this response in the part and this capability, the failures that you are going to experience are represented by the intersection of those two probability distributions. Looking at it another way. If you establish some acceptable probability of failure, some real low number like 0.001, not 0.02 as in today's systems, you could find what is a true margin. When we do an analysis, our best hope is to calculate this number and if we study failure criteria real hard, our best hope is find this number. This will give us an apparent margin if we did an analysis. The standard way of doing this kind of thing is to apply a factor of safety, where you crank up this response that we carefully calculated by some factor of safety and then compare it to the capability and then you get a margin of safety. One big thing that is missing from what we are doing is addressing the variability in the material capability and the variability in the response of the material. Both variabilities are important. The variability of the material could create different responses.

Let's look at what your group is doing, or at least my idea of what you are doing. I think one of the things that you are doing is determining the variability of all measurable attributes of the constituent. You are trying to relate constituents to components, mainly from an intuition and partly from a scientific or theoretical point of view and partly from a statistical correlation point of view. In these studies, you are also working on establishing specifications. Product uniformity comes about by

enforcing those specifications. I am just trying to state what you are doing and I think it all relates to material variability.

The SPIP Task 3.1 and 3.2 related areas involve product uniformity and variability. The components are not the same every time they are made. Test methods and data address product uniformity. Constituent test data variability is kind of a measure of that nonuniformity. It could be useful to our work in that it would provide us with a statistical database. In the data area, one of the things that we need to try to do as a team is to establish some relational databases that relate to the kind of test data that your group is concerned with and the test data that we use and part performance. In the end we want to try to relate constituent test results to composite performance. We need to observe relationships in order to give us physical insight to help both what you do and what we do.

Pinoli — We are trying to figure out how the constituent influences performance.

Crose — The problem I see is that, yes, that is your emphasis, you are trying to predict performance based on the kind of measurements that you make and your intuition and theories. You leap frog over us and we are in the same game. We are trying to predict performance, too, based on the measured composite properties. I think there is a dual purpose and there should be some flow-through.

Here is another way of thinking about things. You look at variance due to one single constituent property. It might cause a variance in the response and a variance in the capability. You look at another constitutive property, it may relate to a different variance in the response and a different variance in the capability. The problem is when they both happen at the same time, what happens? We don't know how to add those things up.

One key, this is what I think we need, is that we need to be able to relate constitutive properties to what I call fundamental variables. I would like to distinguish something that is measured on a specimen of the material from something that you do to the material to make it. Basically what I am saying is that there are fundamental variables that influence your constitutive properties and eventually system performance. Fundamental variables really count and those are the things that you

control. I think one thing that we can do is to start finding out how fundamental variables affect both constitutive properties and composite properties. When you get into that and you look at the overall scope of where you have to go to get a good science base, observe the hierarchy of data, which is also the fabrication process. You start out with some raw material, then there are some manufacturing variables, you do some testing on constituent properties and then in the cloth form, there are some more manufacturing variables, prepreg form, more manufacturing variables, etc.. You keep building the product with various levels of manufacturing variables, which I would call the fundamental variables and constituent properties at each level and finally down here we have composite properties. Then we add on to that all the environmental variables and finally nature brings us down to part performance and its reliability. This depends on everything we did to the material over here. As scientists and engineers our job is over here. At best we take constitutive properties at the various levels. At worst as designers, we take composite properties, environmental variables and this then is the Task 3.1 job where we work with these properties and these loads and try to predict part performance and reliability. We missed a big part of the variability part of the question. We need to relate manufacturing variables to constituent properties in such a way that you can feed it in to the science and engineering that goes into predicting part performance.

Pinoli

This is not just a one way street. You are looking at the composite and trying to identify the critical parameters that you feel will affect performance. Once you have done this, we can go back into the constituents and manufacture constituent that will provide consistent performance.

Crose

One thing is that there are large amounts of data continually developed and I never see it. If you look back on the previous chart, there are 6 levels of relationships and we tested everything against everything else and there were 4 individual tests and three manufacturing variables at each of those 6 processing levels and if you wanted to count 3 different values for each of the manufacturing variables and do three replications, the number of data points would require 26,000,000 experiments. At $500 each, it would take $13 billion dollars to do that. That is ridiculous and there is room for experimental planning that is intelligent to reduce the scope of the problem and I think there is a role for a computerized database and query tool needed to handle the data.

What I am recommending is relating manufacturing variables to constituent properties and composite properties and build up the relationship all the way down the line. One thing that can help is to search and find microstructural features to aid in developing relationships, I call this a physically based model. You try to find in the microstructure, the finished part, flags that relate to the manufacturing variables that went into the part. Julius Jortner and others have done this kind of thing very successfully. We need to develop a statistically based predictive model to relate manufacturing variables to part performance. We need to establish a computerized material property relational database to facilitate the required studies and correlations. One thing that you could do rather quickly and should start thinking about is the storage of information that you create as time goes on. Every time you run a test on a material at whatever level, it needs to be associated with the product number, certification number or what have you and entered into the database. These things need to be collected for months. years, and with the right kind of query tool, you could start to do some of these studies and do them in a cost effective, responsive manner.

Pinoli — Thanks, Greg. I think we are now going to have some complimentary words from Eric with regards to 3.1 activity.

Stokes — What I would like to talk about today is selection of acceptance tests for cured carbon phenolics. In the past, we have looked at constitutive testing and we are now talking about going into tag end testing for cured carbon phenolic materials. What I would like to talk about is a proposed process by which to select acceptance tests for cured materials. What I am not going to talk about is SORI's capabilities in testing and what we do and I am not going to be recommending any particular acceptance test. I want to concentrate on a process for selecting acceptance tests.

What are some of the desirable properties of an acceptance test? They are very similar to what you are looking for in a constitutive test with maybe a couple of exceptions. I think primarily what we want is a test that is going to predict when we are going to see failure, or in some way relates to performance. That is the number one thing we should be looking for. Number two, it should be a discriminator between good and bad materials. What I mean there is that it should be sensitive enough to pick up what you need to know about the material and whether or not it

is going to perform good or bad. Then of course, accuracy, precision. The test should be able to be performed in a timely manner, minimal cost, simple for people to perform, and then finally if at all possible, it would be nice to have a material property. The reason for that is you can relate this large data base you would be generating to other data that is in the literature or even relating data from one part to another, which you can't do now.

What I have done is divided up the primary failure modes, or lack of performance modes, for carbon phenolic, and then put down a series of primary and secondary factors that may be governing those events. I would like to come back to this at the end. First I would like to cover each one individually.

First is erosion rate. I am pretty sure most of you know what that is. It is just the loss of material at the flame surface as a function of the total initial thickness of the material. Of course the optimum thing would be to have very little erosion. What I have done on these viewgraphs is put down possible results of bad performance as far as erosion rate and then again spell out the properties that result in a high susceptibility of that event. Essentially you are looking at lower margins of safety and changes in throat diameter of the part. Lower carbonization temperatures and higher resin contents are generally going to result in a higher erosion rate. Now as I go through these, I would like to emphasize that this is my perception of why these events occur and I know you will have a lot of additions.

Char depth, or the heat effected region, is just that region that is heat effected below the erosion line of the material and ...

Ismail I have a question here. You are putting the emphasis here on the carbon that comes from the carbon fiber but you do have a char there which could have much more graphitity than the carbon fiber. Why are you putting the emphasis on the firing temperature of the fiber and ignoring the properties of the char of the fiber. That is going to affect a lot more, your erosion.

Stokes That is partly governed by resin content and the type of resin. When I put this together, I was thinking of one resin system for, say an RSRM situation. We are not talking about a PAN versus a rayon fiber, or one resin system versus another. These

are just variations within one system. This is what acceptance test is all about anyway.

Char depth, again lower margins of safety, destruction of the adhesive on the back face of the carbon and back face gas pressures driven primarily by higher thermal conductivities in the material which relates back to the fiber and higher heats of pyrolysis.

The next one is pocketing. This happens when you have a ply layup pretty near 90° to the flame surface. What happens is, you go through, at the high heating rates that are seen in the nozzle, a large accros ply thermal expansion driven by pore pressure which results in a high across poly compressive load being applied to the material. Thus large across ply compressive stress shuts down the in plane permeability of the material. This is in plane permeability, the ability of the gases to move in that direction, as a function of temperature and also as a function of that across ply compressive stress on that material. As you can see, as you get up to higher across ply compressive stresses, the permeability is driven lower. What happens is the pore pressure goes up and eventually the pressure, which is a hydrostatic type pressure breaks the in plane fibers and you get failures.

With the result of pocketing, burn through, higher erosion rate, destruction of the flow field. Things that result in a higher susceptibility to the event are lower yarn strengths, lower elevated temperature, in-plane permeability as a function of across ply compressive stress, higher across ply thermal expansion, and lower char yield. These are some examples, the most notable being the STS8A.

Pinoli — You have said something that really bothers me, reported across ply thermal expansion. It is not really composite expansion.

Stokes — It is really pore pressure induced.

Pore pressure does sometimes rely on the across ply thermal expansion. If you have a higher expansion rate, it closes off those pores.

Pinoli — Anybody that talks about CTE as a material property is being misled by the pore pressure effect.

Stokes — Okay. Plylift. Most of you are familiar with plylift. What happens is you have across tensile failure at simultaneous locations at one isotherm in the material. That failure event has been shown to occur at 500° and is associated with the permeability of the material. If you rotate the material to higher angles, you get rid of the event. If you rotate the material to lower angles, the event is more pronounced. This is just to show you some room temperature permeability data. These represent the material identification numbers down here. There are probably 50 different materials, RSRM materials and you can see the variability in permeability. This is about 5 orders of magnitude from there to there. We looked at several different materials and they have different across ply tensile strength curves as a function of temperature. We found that the event in all cases occurred at the cross over of the across ply tensile strength and the vapor pressure curve of water. This indicates that the event is happening due to the pore pressure produced by water vapor.

The other thing that we have done recently is to correlate this permeability with this closed crenulation channels that we found in the reinforcing fibers. This permeability has been measured as a function of temperature and is constant from room temperature up to roughly 500°F. We think that the permeability that is driving this event is related to the room temperature permeability and closed crenulation channels in RSRM material. What this graph shows is, if you take a permeability specimen out of a homogeneous materials and you machine it down to various thicknesses, the permeability of a material is independent of its thickness. It is a material property. What you find is in carbon phenolic materials is that the permeability increases as the specimen thickness decreases. The reason for that is that these closed crenulation channels are of fixed length. As you reduce the thickness of the specimen, you open more and more of these permeability channels. That was sort of the conclusive bit of evidence that we used to document that it is closed crenulation channels and not interface permeability, microcrack permeability and, we don't think, porous fiber permeability.

Pinoli — You don't see much evidence of voids in North American fiber. We can make a case for the fact that the permeability in North American based carbon fiber

composites is therefore low. Unfortunately, if you go back to the AVTEX production, it was all over the map. It varied from no voids to high void content fiber. How can you clearly define the problem of permeability when AVTEX yarn varied so much?

Crose — Remember the 5 orders of magnitude.

Stokes — Right.

Pinoli — Okay.

Bhe — What happened to resin contribution?

Stokes — To permeability? We don't see any contribution. If you look at the across ply permeabilities of these materials, it is down below $10^{-20}cm^2$. You can't even measure it.

Towne — Eric, I am having trouble with the centralization of the permeability being so sensitive to pressure and temperature of your specimen which I think, I just have trouble visualizing the mechanism.

Stokes — This is only at low temperature. This is where the permeability is made constant as a function of temperature and pressure.

Indulge me just for a few minutes. Let me run through this quickly. I gave this presentation at JANNAF and it shows the evidence for the permeability being the closed crenulation channels. This is just the latter part of one of the papers, the first thing we see is that the across ply permeability is orders of magnitude lower than the permeability of the material in the plane of the cloth. This data indicates that the permeability of the material is in the plane of the cloth.

The next thing is, we don't see the microcracks in fully cured RSRM type materials. They're just not there.

Towne — Do you have a pedigree on that material. To me that looks a lot like old AVTEX.

Stokes — It is. We don't see any microcracks.

Towne — I see that you don't have microcracks.

Day — The permeability drops when you heat it up. Where is the hole going when you heat it up?

Stokes — It's in the fiber, right? This is the data that you are talking about, right? Here is the permeability of the material and here is the sensitivity of our apparatus at elevated temperature. The permeability of the material drops off around 500°F. This right here is so close and if you are familiar with how the data is taken, it is very possible that drop off could have been due to experimental error.

Pinoli — I thought permeability went up as you increased temperature.

Crose — That is at a much higher temperature.

Day — You are talking about the difference between 500° and room temperature.

Stokes — Permeability is a property of the material. The flow rate of the gases through the material actually decreases at elevated temperature because the density drop in the gas. What you are seeing here is permeability and as you are driving up the temperature, you are getting very close to that area where you can't see it anymore and at the same time, the actual flow rates you are measuring are getting lower and lower.

We did an experiment over here where we heat treated specimens in an oven for 16-40 hours, brought them back to room temperature and measured permeability. What you are looking at there is the generation of cracks in the material. As you get up above 450°F, you start generating cracks and the permeability goes up. This is in contrast to the dynamic measurement here.

The next piece of information is we generated in plane permeability as a function of across ply compressive stress. This is specimen we used to generate fill permeability as a function of across ply compressive stress. This is all carbon phenolic here. You

put a compressive load on the top and the bottom, your across ply direction is this way. You are measuring the movement of gases from one of these chambers into the other. You don't see any effect of across ply compressive stress at room temperature on the permeability of the material which indicates that the channel has a very high modulus material surrounding it. That is not something you would expect from a microcracked material.

The next piece of evidence is that across ply tensile strength and permeability are not related. It is just a scatter. If you are getting your permeability through microcracking or at an interface, you expect some relationship between across ply tensile strength and permeability. You don't see that.

Beckley Eric, there is a little bit of data that, in fact there is a lot of data that says that compressive strength and shear strength with rayon fiber has been going up, respectively the permeability has been going down. I think that it is the overall general picture and I believe that they are related. Both of us have encountered increases in compressive and shear that have required spec adjustments to continue to send material. The picture is that we are getting better fiber bonding, less gaping and less microcracking.

Stokes What kind of compressive specimen?

Beckley ASTM-D695.

Stokes Is it in plane compression or across ply compression?

Beckley Across ply compression, excuse me, it is in plane compression.

Stokes I don't know. I'm not privy to the data.

Beckley I'm just saying that I would like you to think about the fact that there is another data set that says there is a relationship for the vast amount of material that has shown those traits. We have had to revise our specs to upper limits to allow for higher strengths. It began to happen in AVTEX and then the NARC has continued on with this higher set of data.

Stokes

This is some data that Tom alluded to before. We took a series of specimens of known permeability and then we heat soaked them at various temperatures for 16-40 hours and then measured their permeability again at room temperature. You can see that the materials essentially remained constant up to around 450° to 500°. Some of the materials went all the way out to 500° with no change in permeability. What that suggests is that if you are seeing flow at the interface then you would expect further curing mechanisms to go on for further curing bonds to be forming. That should alter the permeability that you see. It doesn't appear to be doing that.

This is another experiment that we did. What we had was a facility that measures the permeability through the specimen and we have a vacuum transducer downstream from the specimen and we measure flow rates using ideal gas law.

Let me quickly go through the rest of this. Residual vols is just another name for permeability as we all know. It is that 4¼ hour test that we saw were distinct differences between two yarn vintages for AVTEX which is again an indication that permeability is related to the rayon itself.

This is a plot of residual vols against yarn breaking strength and again there is a fairly good relationship. These outliers here are some material that has been aged for quite some time. The fact that permeability is related to a yarn property is indicative that the permeability is governed by some property of the yarn itself.

This is some helium pyncometry data that we obtained. This is a helium pyncometer for most of you who don't know what it is, or how it works. What you do is you have two fixed volumes and you put your sample in here and pressurize that volume and then you release the pressure into the second fixed volume. Using the ideal gas law you can calculate the volume that the material occupied or the volume of helium that the material displaces. A couple caveats to this are if you have very long tubes or small diameter tubes or pores that have constrictions in them, you have an unstable situation so that when you increase the pressure and close the valve off, you'll see a decrease in that pressure. The same thing is when you vent it off to this chamber you will see an increase in that pressure, indicating that the gases inside are venting out or in the other case the gases on the outside are venting in causing an unstable situation.

Pinoli — Are you talking about carbon fibers?

Stokes — This is the AVTEX preshutdown material and this is the NARC material and you can see that the AVTEX material when you put the initial vacuum on it, the vacuum increases when you shut the valve off and when you put the initial pressure on, the pressure decreases and when you switch to the final pressure, the pressure increases again. There are distinct differences in the actual density that you calculate and the pore volumes that you calculate from the data. There are distinct differences between the AVTEX and NARC material.

Ismail — Isn't this number a lot higher than what you get, Pat? I never got 2, no. I get 1.5, 1.7. This is a very high number.

Beckley — Myles, what do you think that number means? WCA.

Towne — We were using helium on that and we got those numbers.

Stokes — You cut the fabric up into about a 5 by 5 inch patches.

Beckley — With VCL, you get a number that is quite a bit higher.

Stokes — If you look at NARC or AVTEX preshutdown composites at the fiber ends what you see are distinct differences in crenulation patterns. You can see these closed crenulation channels that are very numerous in the AVTEX material.

The next thing we did was we took a series of specimens of fixed permeability, the actual measured permeabilities that we determined on these specimens. This is the Darcy's laws and this is the specimen thickness here. We counted about a thousand fiber ends from each of those specimens and we sectioned them up and examines them under optical microscopy at 1000X and we actually counted the crenulation channels that we saw. We categorized those fiber ends as having no crenulation channels, having one of roughly 1 micron in diameter, 2 microns in diameter, 3 microns in diameter. We then applied a scaling factor to those numbers to get a total scale closed crenulation channel area over here. These are the total number of fibers that we counted and we divided the total number of fibers into the total scale area to

get a scale area per fiber. These are AVTEX preshutdown, AVTEX restart, and NARC. This is the scale closed crenulation channel area per fiber and this is the permeability and the obtained a linear relationship between the two. We expect these points up here and these points down here to be shifted down that way because you have pores that are over three microns in diameter that are going to be undercounted in this region and pores that are well under 1 micron in diameter are going to be overestimated or overaccounted for in that region.

Ismail — Is that log scale?

Stokes — Log-log. These are log numbers here. This is 10^{-12}, 10^{-13}, 10^{-14}.

The final piece of information that we came up with is if you look at the relationship between permeability and specimen thickness. Permeability is a material property and doesn't change with the thickness of the specimen that you are measuring the permeability on. If you had channels of fixed length in that specimen and you reduce the thickness, you notice that more and more channels are being opened up and you would expect the permeability to increase. The poco graphite had virtually no change in permeability with reductions in specimen thickness and you notice the increase in permeability with the reduction of specimen thickness with the RSRM material. We did this again for another material here. This is the NARC material and the slope of these lines is going to be related to the length of the channels within the material.

This is why we believe the closed crenulation channels are the source of permeability in carbon phenolic at room temperature. Of all the rayon based materials that I have looked at, I believe that is the source of room temperature permeability.

Bhe — Eric, did you check PAN based fibers?

Stokes — PAN based fibers have a very circular cross section. They don't have crenulation. They have high permeability because they are highly microcracked.

Here are some reasons why the correlation isn't perfect. One is that the variability in cross sectional area within the part. You see variations in the crenulation pattern.

This is a schematic of a material that we looked at that is actually from AVTEX tag end and these are individual plies and the yarn end that you see. What I am going to do is show some pictures of these locations to show you that the variability that you see in these materials as far as closed crenulation channels.

You will notice the lack of closed crenulation channels here and here and these highly cremulated areas here. That is just these three locations here, one ply apart. If you go down the ply, you see the same highly cremulated, a lot of closed crenulation channels all the way through the ply. You could have adjacent plies that vary highly in the closed crenulation channels that you see.

One of the results of this could be localized internal high pressure areas and you could see a structure like this develop. The next thing is variation in length of the crenulation channels. Even though you see a large number of crenulation channels in the cross section of the materials, if those channels are short in length, they don't traverse from the gas generation zone to the zone where the permeability of the material is high and you could still develop pressures in the material. If you have plugged channels when you treat the fabric and are not controlling the viscosity of the resin that you are putting on, you can have variations in how much that resin wicks up into those closed crenulation channels.

We talked about deposition in the pores themselves. I tend not to put a lot of faith in this because it is a fairly high temperature process, but it is possible that you could clog the pores by generating some high molecular weight organic that gets into the pores and somehow plugs it up during the actual firing event.

Finally, as we have seen, there is quite a bit of variability in the stability of the matrix. This is the same plot as where we heat treated the permeability specimens at various temperatures and looked at the development of cracks sufficient enough to generate this increase in permeability. You can see materials that go all the way up to 500 and don't develop any microcracks and other materials back at 430°F that are, so the stability of the matrix itself may be a factor.

Back to ply lift. Essentially lower room temperature, permeability, lower across ply tensile strength and to some extent higher volatile content are the things that contribute to the occurences of the event.

Day — I think this is all really good data, but how can you say that lower room temperature permeability means anything in plylifting in those materials there. Those are high permeability materials.

Stokes — We don't know that. We never measured the permeability of those materials.

Day — They had some fairly high residual vol numbers.

Stokes — We went through those 5 examples...

Day — The next one is TEM-7 and TEM-8 were measured and also were measured at having rather low permeability. They did not perform like those, they looked rather good.

Stokes — TEM-7 was around FSM-1, but the FSM-1 and the 15B were the lowest permeabilities that we measured and they did plylift. There is a correlation.

Day — TEM-7 and TEM-8 are NARC materials that are measured at low room temperature permeabilities and also low residual vol content. They did not show that event at all. My question is, I love you data, what are we going to do about this nasty gang of facts here?

Stokes — We haven't fully resolved plylift yet.

Day — ASTM has a procedure for doing permeability and I think the number is 1534. They have a discussion for why permeabilities change with thickness. You may want to look into that.

Stokes — Okay.

Day — I think it is on polymer film.

Stokes Okay.

Pinoli I keep going back to AVTEX which did not have crenulation lobe void in their product and that was some of the best carbon fabric that anybody ever saw. For three years of production, I monitored AVTEX. Do you remember how that went, Wayne? We thought that was some of the best product ever made. Then it changed about 5 years later. We looked at it and it had voids all over the place. Then it was coming and going at random. Now there is an inference here that the problem is crenulation lobe voids. Why didn't we have problems with AVTEX, is it possible we did and just didn't understand the performance?.

Crose Eric is talking about room temperature permeability. The plylift event is happening at that temperature where he is just getting past the room temperature type of permeability and starting to have the microcracking permeability on top of it. In that narrow temperature range, closed renulation channels may be less important.

Pinoli I don't have any argument with what is going on. I have an argument with regards to what do we want at the precursor level. I keep coming back to that issue.

Crose What I am saying is that the crenulation channels may not have anything to do with plylift. They may only have something to do with low temperature permeability of rayon based phenolics.

Pinoli I don't feel comfortable with the idea that something about North American's product is inferior. I don't think that is the case. There is one good thing about North American's product that I personally like. It is consistent. That is something we never saw in AVTEX. I think we have to be careful that as we get smarter, we find things of finer detail that may or may not be significant.

Stokes On to delamination. Delaminations are the result, primarily of large thermal contraction that occurs at the higher temperatures. The properties that result in higher susceptibility to the event, higher across ply contraction, lower across ply tensile strength, and lower char yield.

Then there is thermostructural failure. This has been predicted, but we have not seen it in carbon phenolics. Essentially it is high in plane thermal expansion that occurs at high temperatures driving this material into compression and would theoretically form an across ply failure, excuse me, a fiber failure at that location.

Beckley — Eric, are you talking about a particular part here? It strikes me that bias tape, there is no circumferential fiber. The fiber is really off on a 45° angle.

Stokes — This is the last one. Wedgeout occurs at the junction of two parts where you have a ply angle to the edge of the part and you get a thermal expansion with a compressive force driving the part together which generates a shear load on the specimen and you get these little wedges that pop out.

Okay, the last view graph, I promise. Essentially what we would like to propose is that you take all these key properties and line them up and then take the different tests proposed to do acceptance testing and see how many of these properties you can get some insight into and by picking a few of those tests, one trys to cover the range of critical properties that you need. I am not trying to advocate these particular tests, just trying to give you a process that might work in selecting acceptance tests.

Hall — Eric we appreciate it.

Devane — I am here to talk about carbon assay testing. What I am going to go through is a little background of what the issue is, discuss some preliminary work that we have done at BP, and then more detailed work where we looked at two different standards, two different machines, three different technicians and compared results, and then discuss moisture. We found moisture was one of the variables that would significantly affect the result. I will touch on the issue of system capability.

Through SPIP there were concerns about the test precision and accuracy. There was variation noted from lab to lab, machine to machine, method to method, and also some sort of variation over time. Then an issue came out regarding standard selection. Should we use a fabric? Should we use a particulate?

These sheets show some of the results that Pat put together, some round robin tests between labs. The bottom line is this. You have between 0 to 2% difference from lab to lab, method to method. Pat, do you agree with that?

Pinoli Yes.

Devane Finally some other work that Pat, also, put together. He looked at vendor certification. He looked at some results put together by LECO Corporation. Here there was a much more striking difference. Between 98 down to 93%, a very large difference. We were asking questions in Alpharetta, is there some sort of aging going on. That is the background.

We started some preliminary work at that time. Basically we went out and took our current standard and we tested the heck out of it to try and get an understanding of what the system's capability was. How much variation would we see, if we tested our standard as both a standard and a sample? Then we received some results from Jim Suhoza where LECO Corporation had taken WCA and tested it. Incidentally, the standard that we used is from a company called Alpha Resource which is supposedly 99.998% carbon. The WCA is also supposedly 99.9%, right up to 100% material. They should be the same. This is what we found comparing our results with Leco's. The red curve is LECO using WCA with their CR12. The green curve is also LECO results with WCA on what they call an SC444, a different type of machine. When we look at these results, we were surprised that the range with the CR12/WCA and our CHN 600/Alpha standard was identical. At the time we were discussing whether we should use WCA as a standard. LECO said it would "burn like a fiber" and therefore might be more accurate. When we saw this data, we said wait a minute. Something is going on here. We need to do another study. Let's take WCA and Alpha Resources graphite, put them on the same machine and test it. We would then identify possible sources of variation, try to investigate the most likely causes, and then look at the standard selection and ask some key questions. Is one more precise or accurate? We tried to answer the questions, "does it burn differently"?, Does it behave differently if you have a fabric or a particulate.

We set up a test and took 3 technicians, two machines, two standards. Each person was to test 120 samples consisting of 4 trays with 30 samples per tray. They then took the samples and interspersed them in sets of 5 WCA and 5 Alpha, etc.

Here are the results for old and new CHN units, Alpha, WCA and the difference between the two. This is the first tray, Tech 1, the second tray, Tech 2. When this technician did it, he calibrated the machine once to start, then ran 60 samples straight. The next two test sets were done independently. Normally we run every 10th as a standard. We did not do that on this set. We wanted 60 in a row and thirty in a row. The reason you have three for Tech 1 is that you have the average. There are several ways to look at this data.

The first way is just looking at the general distribution. The results that I have here are not really conclusive. There is really no clear winner. Note that we have results for two different machines, called "old" and "new". As you can see, they don't build them like they used to. The standard deviation has almost doubled, but there is very little difference between the samples.

One of the more significant sources of error, and possibly a problem with those early LECO results where we went from a 98% down to 94 or 93% assay could possibly be moisture, aging, absorbing some sort of gas, whatever. We decided to performe a study to confirm the influence of moisture on the results. We looked at carbon assay and hydrogen as a function of sample moisture content. One of the advantages that the CHN 600 has over the CR-12 or the SC444 is that you are able to simultaneously get C, H, and N. If there are ither elements present you will know.

We also looked at the fabric's moisture pick up rate, to see what that is going to imply for the test method. How quick do you need to seal your sample, how consistent must your method be.

This next chart shows moisture content versus carbon assay and hydrogen. Those of you with a chemical background, this is what the prediction would be. As you drop 97% to 89% carbon, and you are assuming it is all water in there, your hydrogen is going to go from 0 to 0.9. In this case we started with CCA3 carbo and conditioned it. The implication here is, if the technician does testing, and does not

adequately dry the sample, you are going to get a low carbon value. You are probably not going to get a false high, but you will get a false low. This is something that you have to consider. It doesn't take much. Two percent moisture and you are down 2 percent carbon, 1 for 1.

Beckley Was this WCA?

Devane No, this is CCA...

Beckley Did you try them at random?

Devane We went out and took a sample into the lab and conditioned it and inserted it into the capsules and ran it.

So moisture is a problem. But how quickly do we need to seal the capsule? How easily can we screw up the result? We looked at exposure to the atmosphere at 3 different relative humidities, up to 20 minutes in time and we looked at the weight gain that you would get. These were the results. Within 10 minutes, you are at 2% moisture. Our conclusions so far are firstly, there is no difference between the two standards, and secondly moisture can bias the result, and therefore your technique has to be good enough so that you get a sample into the capsule quickly. In fact, even if we seal our capsules quickly, if we don't test them right away, and I don't have numbers on this but this is the technician's opinion, they will pick up moisture.

Let's step back and look at the whole process. We are going to calibrate the machine. We are going to have some probability of getting exactly the correct assay value or lower than the correct value or higher than because the machine has a certain capability. When we then add to that, the variation of testing some unknown sample, you have the same situation. Someway or another, even if there are no impurities,you are going to have variation. The derivation for an unknown sample could be wider, even if the sample is "pure" because we are combining the process variability due to testing the standard with the variability due to testing the unknown. When you look at the standard deviations that I showed earlier, they are simply the effect of one of these two, and not the combined. I would expect double the standard deviation when you look at an unknown sample.

To give you a better understanding of this issue, this is a run chart for our testing on the old CHN unit. Between each of these vertical lines is data for one tray. Here are all 6 trays. Here is the first 60 that were run in sequence. Alpha is the red and WCA is the turquoise. It is relatively uniform and if you were to make a histogram of that data, you would expect something that looks like this, but hours later somebody comes in and calibrates the machine again. Probability says that with 3 randomly selected results 12% of the time the calibration used will higher than the average. The next person comes in and calibrates again and again. When you look at the total population, your data distribution is going to be more like this. Another way of looking at it is system capability. Just assume we have something like this. Assume you have an actual assay of 99.9. 50% of the time, you are going to higher than actual. 50% of the time, the result will be lower. Twelve percent of the time the prior probability is that 3 in a row are going to higher than the average. It is interesting to think that in ASRM we are going to have a lot of carbon assay results which are more than 100%. You have 101% carbon on this one. This is impossible, but if you throw out the high data, if you say it can't be 101, you are throwing away this whole half of the curve. What we want is the whole population. We must average it in instead of throwing it away. When you see a cert out there one day that says 102%, don't complain.

In conclusion, for the standard selection, we are going to continue to use the Alpha unless otherwise directed by a program. If someone wants us to use something different we will, no problem.

We are going to be looking at machine and technician variation further. The moisture can cause significant variation. Whatever test procedure we use, it has to mitigate the effects of moisture. The drying procedure has to be pretty tight if you want to have consistent results. In addition, we would recommend using the hydrogen number so that if you get hydrogen to high, you know that you have to retest due to moisture. Thirdly, how do programs want to handle numbers greater than 100. The assay procedure is not that sensitive. There is a lot of variability in it as there is in any test method. How do handle that? My thoughts are that we should handle it with SPC, 3 or 4 results, make a run chart, generate upper and lower spec limits, and look for trends. The system that we are monitoring consists of two things. It is the firing process itself and it is the assay testing. When we see

an unnatural pattern there has been a change. What I think you are interested in here is for a qualified ongoing program. You don't care whether the carbon assay is 101 or 102, or 98 or 97. You just want to know it is the same. That is always the same. That concludes my talk. Are there any questions?

Pinoli — I have a question. On this particular chart, did you introduce moisture into the same sample.

Devane — I asked the technician to take a sample and condition it. The reason it is not really neat steps is she would condition it, test it.

Towne — Is the material that you used here the same that you used on the chart?

Devane — On the moisture? It was fired at the same condition, one was CCA8 and the other was CCA3. The same conditions, just different rayons.

Towne — The 97% material was picking up moisture.

Devane — Yes. The CCA3 is AVTEX based and the CCA8 is NARC.

Ismail — I look at your high moisture content, 8% water plus 86% carbon, that is 94.

Devane — Let assume we have a ratio of 9%.

Ismail — What is your carbon?

Devane — This is 97.

Pinoli — To try to measure the exact content of water in that sample is a difficult task. If you place the sample on a balance, the weight continues to increase.

Devane — Yes, it is gaining all the time. It is not perfect, but it is close. I think I'll jump down now. Thank you.

Drake

We are going to the data base demonstration now. The data base that I am going to demonstrate to you was developed by WIDC at Oak Ridge Laboratories and was developed for the TOP program. About 3 or 4 months ago, I was in Huntsville talking to Cindy and Pat and they kind of liked this data base or at least the thought of it. I made a copy of it and I sent it down to them, and they liked it even better. They suggested that I give you a demonstration on it. This particular data base can be updated on a periodic basis by giving them your old disk and they will give you a new one. The example is the new concept for an ablative data base, although what you will see is not ablative data. I would use it to create a data base for all of the constituent material. Example, vendor specifications, appropriate properties in conjunction with the SPIP program. I might add that we are looking at it at Aerospace in order to create A level values in conjunction with some of the things that have been happening with SORI and so forth. We have put in for an Aerospace funded program that we think is going to be approved. Let's adjourn and go over to the computer room.

Pinoli

Now Les Tepe is going to tell us a little about the Phillips Lab.

Tepe

I have been asked to give you an overview of the composites laboratory at the Phillips Laboratory. The Phillips Laboratory was formerly the Air Force Laboratory. The Air Force has gone through several reorganizations recently in the lab structure. The intent of the organization was to reduce the number DoD laboratories to try and streamline the management and make things simpler. The rocket propulsion laboratory was involved in supporting propulsion for all kinds of propulsion applications all the way from air launch to space to ballistic motors. We had part of that charter moved from us to the Navy in the way of the air launch application. Our customers that we knew are different. The customers that you knew through us are somewhat different and all I can say is stay tuned and see what happens in the future.

What I am going to present to you this morning is an overview of the composites laboratory at Edwards Air Force Base. The Phillips Lab is a conglomeration of people and processes that are trying to understand each other and trying to work together. Our particular operating process, we budget money from different categories, and locally our travel will be managed under one pot, but our program

money is managed in a separate pot, because the management is coming out of Kirkland, we are doing it their way.

The reason we got into a laboratory was our organization had a bimodal distribution of people. A couple of years ago, the senior people at NASA labs realized the people who had experience were disappearing and the young people did not have all that much experience. They wanted to put in place something that would help people get experience to deal with you as customers and be somewhat equal in having the capability to know what we are buying and asking for. We put together this composites laboratory and it was built around 2 components, nozzles and cases. Out of that has sort of grown some other sections and some other work. Buzz Wells from the case side and myself from the nozzle side were involved in structuring this thing and focusing it and it has grown beyond us. There was a push to go more with inhouse people and so our composites laboratory has become a gem in the remanagement and restructuring. It receives a lot of interest. It has always been undermanned and understaffed. We have people limits on what we can do, so we struggle, but I think we have some good work.

Out of this laboratory, Ismail has been involved in the middle of it and has produced some work for this environment and a lot of papers. We have a few other gems like Ismail in the lab.

Physically, we have a 40,000 square foot building which initially was an assemble building that was built by NASA for a Rocketdyne contract to assemble F1 engines that put the Apollo moonshots in place. We have scrounged and recovered resources from lots of places to put this place together.

We have gone beyond the nozzles and the cases. Next door to this plant is our space structures lab. On the composites end, we don't have a lot of different things, but we have some nice things. We have tried to go after top end items, so that we can understand what the current technology is and maybe build on that and maybe transition some of that and interact with as many people as we can. This one was acquired to look at large space structures. This has a 6 by 6 profile window. We have plenty of room. If anything, we have plenty of space up there. Within the ablative part processing, we have a graphite furnace we can use. In sizing this, we

wanted to be at a size where we could understand the problems you have with manufacturing, but not be at a real small size. We wanted to be at an intermediate size that we could understand the manufacturing problems, but not get in the undersize or oversize problems. Everything is sized to make an exit cone about 40" diameter by 40" high. The case side is such that we could make a small ICBM, first stage, if we ever were to do that. People-wise, we will never make anything of any real consequence. We just don't have the people to do that. Some of these pictures, the people have uniforms on. The people are there for the most, three years. The first year they are in training, the next year we can get something out of them, and the third year, they are looking for their next job. It is hard to have a long continuity with military people. We also need to give them that training, so they can become the buyers of your product.

We have some NDE capabilities. Our size that they are looking at are roughly 2 foot by 2 foot. We are involved in the CTE activity for SICBM and as part of that we acquired a work station similar to the work station for the computer tomography inspection system that is located here at Aerojet. We were able to get a small CT system for that and we will be able to look at nozzle components.

Drake What is involved in trying to get something tested.

Tepe Talk to Bill Hildreth, Ross Wainwright. We are not up and running yet, but if you are interested, we would like to work with you.

Besides Ismail, in the way of researchers, as far as doing some real work, we have University of Dayton personnel onsite and that is where Ismail comes in. Dr. Peter Pollock has been working structure mechanics of carbon-carbon primarily and he has cooperated on some of the work that Juluis Joitner did with the crimp angle and material strength. He is going on and trying to work on the interface of the fabric. We have a few others that are working these kinds of things. Beside this work, we have some film work going on for bearings for liquid engines. I am not involved in the carbon-carbon work like I used to be, so I am not as familiar with it as I was at one point. We have Wes Hoffman looking at surface features of carbon fibers and carbon spectras. He's been working under a microscope and looking at how you affect the carbon structure, how do you affect its oxidation resistance. Some of the

work that he has been doing, he started working with small microtubes and we are looking at this work to develop very small injectors and very small heat exchanger. If you haven't been to our place, please come by. Okay, that is what I have to say.

Drake — I would like to introduce Dave Sutton. He is the Director of our Material Evaluation Laboratory at Aerospace. Dave is going to be telling you what we are doing and what our capabilities are at Aerospace.

Sutton — Thanks, Ken. For those of you who don't know what the Aerospace Corporation is, it was spawned in the 60's to basically provide technical support and advice to what has become the Space Systems Division. Part of that company has been the laboratories, or now technology centers. I am in one of those called the Mechanics and Materials Technology Center. We really have two missions. One is to develop new technologies related to space and the launch vehicles and satellites. The other is to provide support, failure analysis, risk assessment, because the company has the overall mission of certifying flight readiness for launch vehicles and payload satellites.

In these technology centers reside the real laboratory capabilities for doing analysis. What I have tried to do here today is provide a survey of those capabilities that we have which would be appropriate for this SPIP activity, what we could contribute to that if asked. We would have to arrange for some sort of Air Force funding if we were going to participate, but we have a lot of capability as you will see.

Although our primary customer is the Space Systems Division of the Air Force, we certainly have had cooperative programs with both NASA and JANNAF. Our most recent program with JANNAF involved us in a round robin where we analyzed hydrazine fuels because they had qualified a new supplier. Currently with NASA we are participating very heavily with the LDEF which is a long duration exposure satellite. As part of this program we are putting together a data base in cooperation with NASA so we may have some commonality there.

I have focused mainly on what we can do with testing prepreg material and cured specimens. I have left out the things that we could do for resins and fibers although

we have a lot of that capability as well. I basically have divided it into these categories.

I am going to diverge a little on this nondestructive evaluation because we are developing a couple of capabilities that I didn't predict would be of interest to this group, particularly the microballoons and a small program we have in fault recognition which might be appropriate for inspecting fabric. That I will adlib.

This is an editorial. I had to put one of those in. This is an advertisement.

I should say that this does not represent the capability of only my department, but I have input here from the composites group, our polymers group, and our NDE group. These are a list of the things we have in the laboratory or tests that we have run for other programs and characterization which could be adapted for a prepreg test.

I think these tests are very important if we want to get at erosion because the residual volatiles moisture has a high impact on chunking. We are capable of doing some mechanical tests that would determine the contents of the material. We can do hardness, porosity a couple of different ways. We have several scanning electron microscopes as well as other surface analysis tools which we use.

We actually have built our own dilatometer that has a very high temperature capability and sensitivity. This is a schematic. It has a 3,000°F capability. Sometimes we get over-enthusiastic and we build our own instruments. I wouldn't recommend it.

This is the advertising part of the talk. I think on the first day we had a real good example. In particular the technique of thermal gravimetric analysis with a very small samples. If the material has homogeneities, the results you get can be real fouled up. In the case of cured samples, people in our laboratory feel that tag ends are not the best. If test parts are designed up front, I think you are much better off.

We also have an ultrasonic capability. This is our NDE group. They have a 4 point false echo, portable unit which can see flaws in materials under ideal conditions of

about 0.1 mm. We use thermography a lot on solid rocket motors because it measures the density and you can look at delamination down to the order of the thickness of the material. Thermo involves a heat source which is changing and you can literally see through the material. Recently we had the occasion to apply this to a section of an upper stage, which in being transported suffered a head-on collision with another semi. This technique was used and we could tell them with a great deal of confidence that this part had not been changed and could be used.

We have some limited capability in radiography. We have microwave oven size facility which we use for dimensional analysis.

There would seem to be some interest in looking at microspheres and some of our people came up with a real ingenious way of using glass microspheres as a smart material. They use the word, idiot savant material. These materials are really pretty dumb, but they can do one thing well. The thing that the microballoons do really well: if you subject them to a pressure, put them in a chamber and raise the pressure with an inert gas and listen to them, it is like rice krispies, snap, crackle and pop. All the weak ones break first, so if the pressure rises and stops at a certain point, you can go back later and raising the pressure and listening, you find out when you first start to hear it, what the highest pressure that that sample of microballoons has ever been subjected to. The application that we had was to put microballoons in an appropriately designed acoustic canister. Put them around a launch pad where the overpressures were being checked. They needed something that could withstand it and these would serve the bill very well. The trick was to design an acoustic chamber to filter the appropriate frequencies out. They also worried about the pressures of the Titan SRMs. They mixed the microballoons in with a grease or a sealer and then they stacked and then restacked and found out what the maximum pressure was by reclaiming the glass baloons and subjecting them to pressure. I wish I had known, I would have brought that data.

Apparently there is some interest here in characterizing the carbon spheres. If they are impervious to air, there is a possibility that these filler spheres are a witness material, and you can take specimens of cured material and compress the specimens, use acoustic emission and see what the maximum pressure of that specimen was. It might be possible to characterize how many of the balloons have failed. You may

actually be able to characterize the stuff in the raw state by getting that acoustic emission fingerprint. This might provide you with a way to characterize your spheres or use it later on as a witness material. You might even be able to size these things by combining pressurization with a float-sink operation.

Drake — I understand we do have some of the microspheres that have been shipped out. Hank is doing an evaluation.

Sutton — One of the other things that we are looking into and maybe we should consider it a second step, is automated fault detection. In a large Titan tank we have these welds that might be 30 or 60 feet long and they are x-rayed. People are pretty good about recognizing flaws, but they get bored very easily. The thought here was to use a lot of the software. These x-rays are easy to digitize. You put these in a two-dimensional microdensitometer scanner or photodensity scanner and you have a digital image of the thing and the computer can go through and pick out anomalies. We have a small internal R&D program that is aimed at that. A lot of the software that we are adapting from have all kinds of filters and codes detecting changes and differences between photographs. We are trying to build on that. Gloria recommended that. There is a small company doing that same thing, digital video imagery to detect faults. If you are looking for bends, warps or flaws in fabric, this might be something you could automate to the extent that it could be done very rapidly and in a continuous fashion.

Drake — We use the same technique to evaluate some Air Force NASA hardware for acceptance. In one case, we had a NASA motor, space craft, in orbit with an anomaly and ended up with 7 nozzles to make 7 flights with no alternate and they x-rayed every 15° to enhance reading the thickness of the material, because the thickness of the composite was of great concern. We were able to read the thickness of these every 15°. It was very effective.

Sutton — It was highly accurate, much better than the eye. This is a good application. As I recall there were two out of family.

This is the advertisement part. We have a unique apparatus at Aerospace Corporation which consists of a 400 kilowatt arcjet and the pumping stations to

evacuate it. It is capable of providing 10,000 BTUs per square foot per second on a target in the path of the jet. We have used it for uniform heating of samples of 0.5 by 2 inches in dimension. We have also used it on stressed samples to measure properties of carbon-carbon composites. This equipment comes with diagnostics which include a fast framing video and recorder. You can measure ablation, or record chunking. It also has fast temperature monitoring via rapidly read thermocouples and two-color pyrometry.

Drake — With the camera you can make a real time picture and when a firing is over you can go right back and look at it.

Sutton — I have one more view graph that summarizes some points I tried to make. We would like to see, if we get involved in any functional testing, a program which would correlate well-defined or well-characterized material. One approach might be to take the properties that you think would effect erosion the most and characterize them and try to correlate them with an erosion test in a very controlled way. With this approach, you might be able to use a functional test to get to a minimum set of tests enabling you to predict properties with accuracy. That is my presentation. Thank you.

Drake — Due to the current economy the Air Force, there are a couple of terms I should explain. One of them is step design. A step design is when you take something and modify it blindly to give to the next configuration. You make some improvements that you think are nice, but they don't really, they are not a major change. The Air Force has been doing this on satellites and launch vehicles. You start all over. You have new ground rules as you are doing in ASRM. Those are pretty few and far between in the Air Force.

With that thought in mind, I bring some issues and concerns that we have. I think you all will recognize the one at the top of the list. I think we tried to make it such that we had traceability all the way back to the rayon mill and the individual lot and in fact we do, but we get that another way. We get it through the documentation packages. Aerospace goes out and very meticulously reviews all these log books, all the hardware to make sure everything is in order. One of the things that we do need to know readily is what type carbonized fabric we have. We assume that you are

using the same resin, the same filler, but in the case of each of the carbonizers, we would like to know if it is VCK, CCA3 or VCL, or whatever type fabric. I'll leave it at that and I will take back the information that I have and hopefully I can put something together in my mind and what I am thinking about is to propose a commander's policy which would go out on all Air Force programs.

Environmental concerns is an area that we are all aware of and I think I have seen one that was raised yesterday. That is the sizing on the rayon. Left untouched, it would come up in four or five years, it would come up an bite us and we would have programs in trouble. I open this up to the floor as to how many other issues are there out there that we should start tracking and being interested in that are EPA or OSHA related that might result in a shut down if we don't do something about them. I would invite you to talk about it now or talk to me offline or write me a note.

Pinoli — I would like to express a comment. When it comes to environmental concerns, it goes across all program lines. It is not just a concern on a DoD program or a NASA program. I think the issue should be addressed in a cooperative manner and it will need a sponsor. You need an organization that will pull this together or each one of the programs will have to fight them separately and it will cost a fortune. Somebody must stand up and say, "I will be the sponsor of this effort and pass the information on to all the programs." My feeling is the industry and customers will be more receptive to accepting the results of these activities, more so than they have in the past. Case in point would be the issue of rayon qualification. The work that has been done by Bob Looney at NARC on rayon was in concert with the NASA organization. I think all of the major DoD programs have just tied right into that. In the past, major efforts would have also been made by each DoD program

Thomas — I think we should write a letter to Hitco, Polycarbon, Fiberite, Thiokol and ask them to identify the concerns that these companies may have. Get everybody to get something on the list.

Drake — I think that is an excellent thought.

Pinoli — I don't think the manufacturer's are going to want to do this work as a freebie. If we can get a sponsoring agent to step up and say it has to be done, and fund it. The

executive committee will take this under advisement and report vack to the full committee at our next meeting in New Orleans.

I think we are now ready for our tour.

APPENDIX A

BOB LOONEY

S.P.I.P.
NOVEMBER 14, 1991
SACRAMENTO, CA

ADVISEMENT TASK 8, ALTERNATIVE RAYON YARN SIZING

OBJECTIVE ELIMINATE NEED FOR FIBER FINISH REMOVAL PRIOR TO CARBONIZATION

PURPOSE

- REDUCE CHLORINATED HYDROCARBON EMISSIONS
- ELIMINATE PROCESSING STEP, THEREBY SAVING COSTS
- ELIMINATE POTENTIAL FOR WEAK CARBON FABRIC BY ELIMINATING OPPORTUNITY

SOLUTION APPROACH

I. PRODUCE YARNS WITH NEW CANDIDATE FINISHES (TWO) IN QUANTITIES (40 LBS.) FOR PLIED SKEIN CARBONIZATION TRIALS OR EQUIVALENT AT POLYCARBON AND B.P. CHEMICAL

- TRIAL YARNS TO BE PRODUCED AT THREE (3) FINISH-ON-YARN (FOY) LEVELS:

  0.10-0.25%
  0.40-0.70%
  1.00-1.20%

- TRIAL YARNS TO BE PRODUCED SIDE BY SIDE WITH CONTROL YARNS (PRESENT FINISH)

- REPEAT FOR REPRODUCIBILITY DETERMINATION

SOLUTION APPROACH - CONTINUED

II. PRODUCE TRIAL YARNS IN QUANTITIES FOR WEAVING FABRIC (320 FOUR TO EIGHT POUND TUBES OF YARN)

- SET UP ONE SPINNING MACHINE TO PRODUCE THIS QUANTITY
- REPEAT FOR REPRODUCIBILITY DETERMINATION

TESTING WILL INCLUDE:

A) THERMOVGRAVIMETRIC ANALYSIS OF FINISH SOLUTION
B) LUBRICITY OF FIBERS
C) STATIC ELECTRICITY
D) BROKEN FILAMENTS/APPEARANCE
E) WINDABILITY
F) PACKAGE FORMATION
G) PACKAGE INTEGRITY (SHIPMENT SURVIVAL, SHELLING POTENTIAL)
H) OFF-WIND PERFORMANCE
I) WEAVABILITY
J) FABRIC APPEARANCE
K) FABRIC CONSTRUCTION SPECS
L) CARBONIZATION PERFORMANCE WITH AND WITHOUT DRY CLEANING
M) CARBON CLOTH STRENGTH, INTEGRITY
N) PREPREG PERFORMANCE
O) FABRICATION PERFORMANCE

III. IF SUCCESSFUL, 1100 DENIER SHOULD BE TESTED AT FIRST OPPORTUNITY.

APPENDIX B

CINDY UPTON

TASK 3: RESIN ADVANCEMENT STUDIES

CURRENT APPROACH

☞ NUCLEAR RESONANCE SPECTROSCOPY

(LIQUID & SOLID STATES)

- ^{1}H, ^{13}C, ^{15}N
- 2D & 3D

☞ CHROMATOGRAPHY

- NORMAL & REVERSED PHASE HIGH PERFORMANCE LIQUID CHROMATOGRAPHY
- PREP SCALE LIQUID CHROMATOGRAPHY
- ION CHROMATOGRAPHY
- SUPER CRITICAL FLUID CHROMATOGRAPHY
- PYROLYSIS GAS CHROMATOGRAPHY

☞ TEST, INC.

☞ SOLOMAT

☞ FOSTER-MILLER

APPENDIX C

TONY DAY

RESIN ADVANCEMENT

NUCLEAR MAGNETIC RESONANCE SPECTROMETRY

A. J. DAY

THIOKOL CORP.

14 NOV 1991

NMR OF SC-1008 PHENOLIC RESIN

- PROTON NMR OF SC-1008 DATES FROM 1964 (CULBERTSON, HIGGENBOTTOM, BARGE, AND REED, "THE DETERMINATION OF DEGREE OF ADVANCEMENT BY IR ANALYSIS"
- ^{13}C NMR ON SC-1008 DATES FROM 1987.
- NMR SPECTRA QUANTIFY HOW COMPLEX THE RESIN REALLY IS.
- NOT A QA TECHNIQUE.
- HAS POTENTIAL FOR SOLID PHASE AND COMPOSITE ANALYSIS.
- CURRENT WORK BEING DONE AT THIOKOL/HUNTSVILLE AND MISSISSIPPI STATE UNIVERSITY (DR. TOM FISHER).

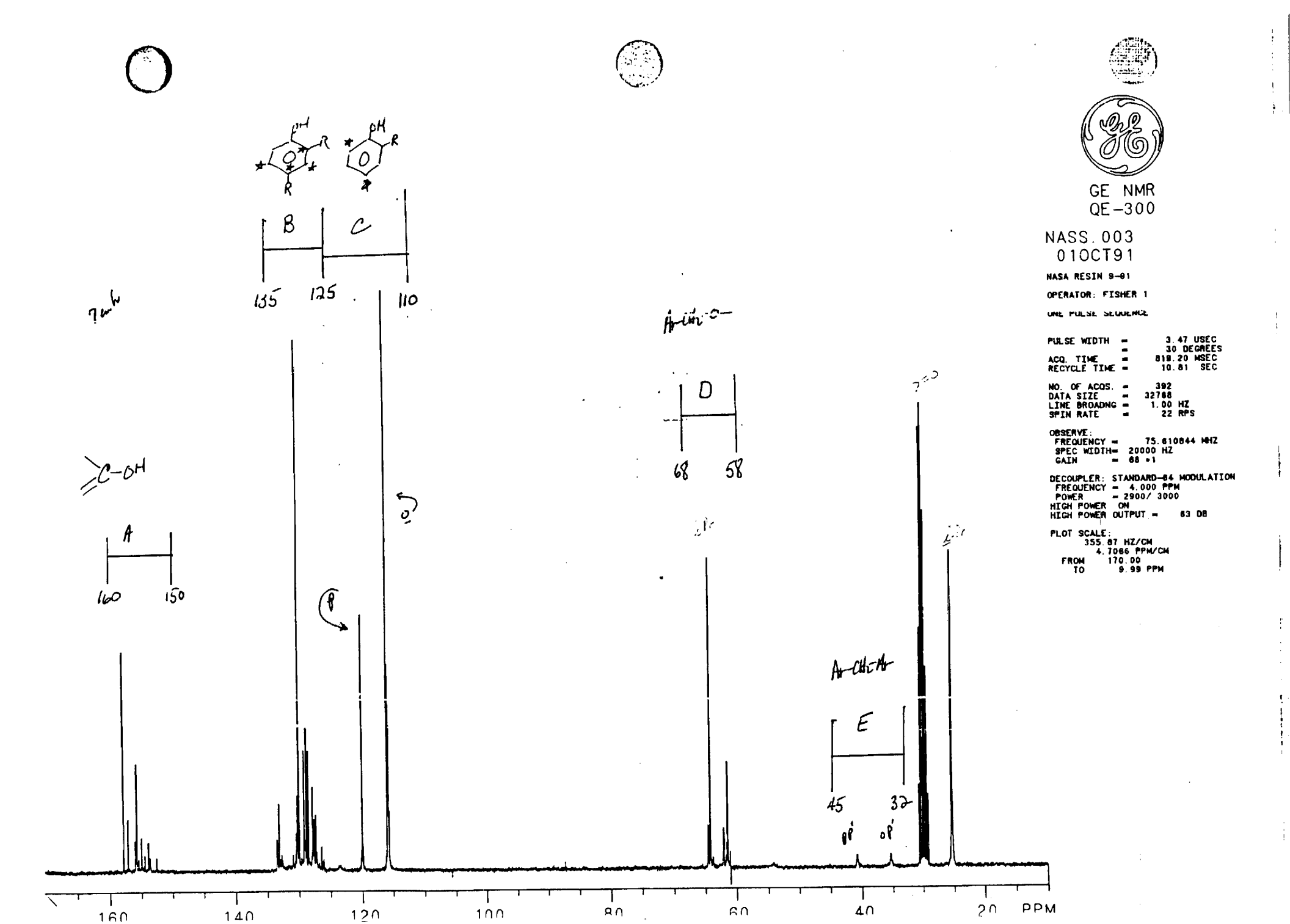
A. J. Day 11 Nov 1991

NMR OF SC-1008 PHENOLIC RESIN

GOALS

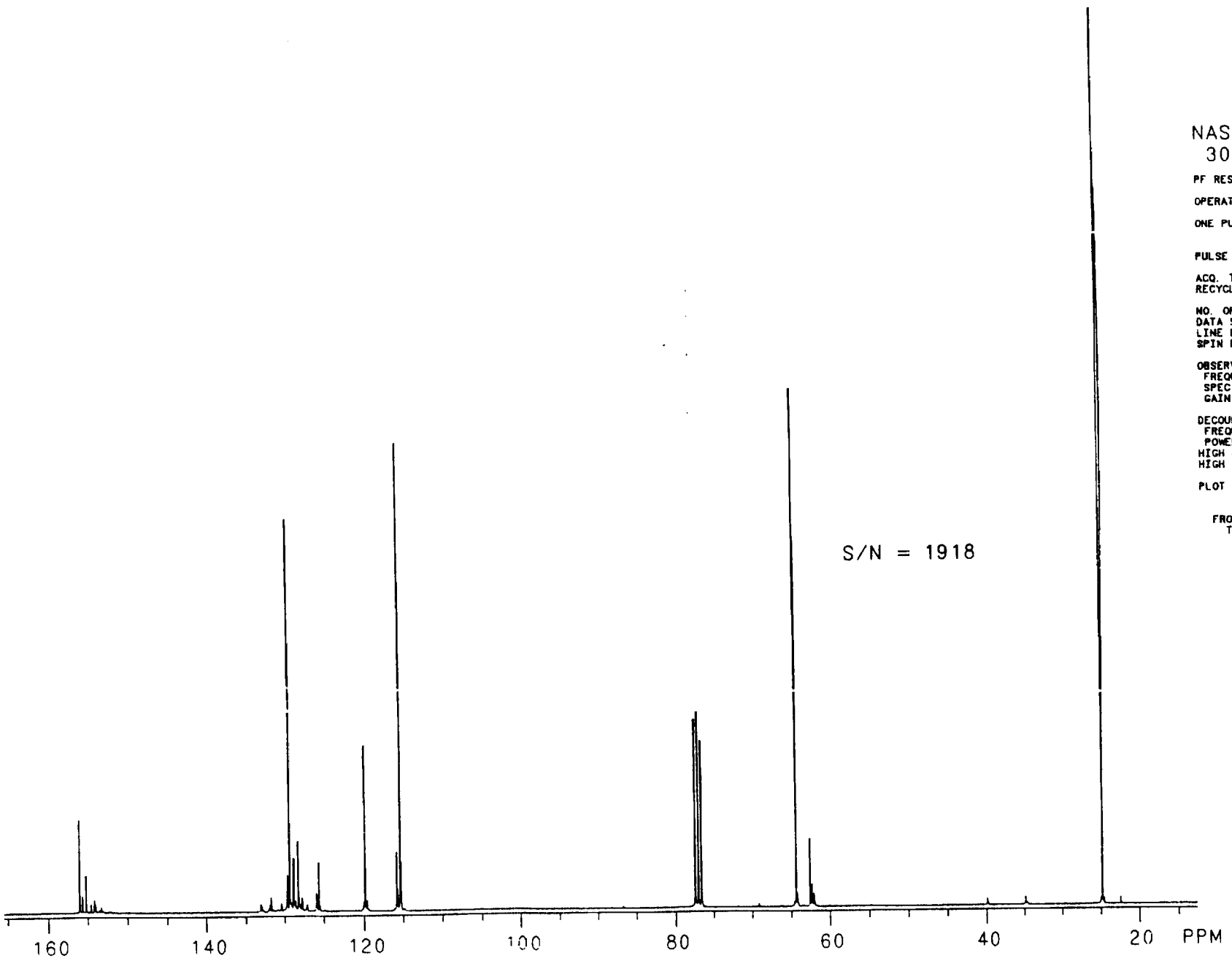
- DETERMINE DEGREE OF ADVANCEMENT OF RESIN IN PREPREG.
- DETERMINE DEGREE OF ADVANCEMENT OF RESIN IN COMPOSITE.

A. J. Day 11 Nov 1991


GE NMR
QE-300
NASS.003
01OCT91
NASA RESIN 9-91
OPERATOR: FISHER 1
ONE PULSE SEQUENCE
PULSE WIDTH = 3.47 USEC
= 30 DEGREES
ACQ. TIME = 818.20 MSEC
RECYCLE TIME = 10.81 SEC
NO. OF ACQS. = 392
DATA SIZE = 32768
LINE BROADNG = 1.00 HZ
SPIN RATE = 22 RPS
OBSERVE:
FREQUENCY = 75.610844 MHZ
SPEC WIDTH= 20000 HZ
GAIN = 68 +1
DECOUPLER: STANDARD-64 MODULATION
FREQUENCY = 4.000 PPM
POWER = 2900/ 3000
HIGH POWER ON
HIGH POWER OUTPUT = 63 DB
PLOT SCALE:
355.87 HZ/CM
4.7066 PPM/CM
FROM 170.00
TO 9.99 PPM
B
C
135
125
110
A
160
150
D
68
58
E
45
32
pp'
op'
160
140
120
100
80
60
40
20
PPM

^{13}C in $CDCl_3$

No O-O' crosslinks found.



GE NMR
QE-300

NASSG.003
30OCT91

PF RESIN IN CDCL3

OPERATOR: FISHER 1

ONE PULSE SEQUENCE

PULSE WIDTH = 3.47 USEC
= 30 DEGREES
ACQ. TIME = 819.20 MSEC
RECYCLE TIME = 10.81 SEC

NO. OF ACQS. = 0
DATA SIZE = 32768
LINE BROADNG = 1.00 HZ
SPIN RATE = 22 RPS

OBSERVE:
FREQUENCY = 75.610844 MHZ
SPEC WIDTH= 20000 HZ
GAIN = 68 +1

DECOUPLER: STANDARD-64 MODULATION
FREQUENCY = 4.000 PPM
POWER = 2900/ 3000
HIGH POWER ON
HIGH POWER OUTPUT = 63 DB

PLOT SCALE:
340.07 HZ/CM
4.4976 PPM/CM
FROM 165.52
TO 12.61 PPM

NUCLEAR MAGNETIC RESONANCE SPECTROMETRY OF SC-1008 PHENOLIC RESIN

SUMMARY

- NO ORTHO-ORTHO METHYLENE FOUND IN THE NEAT RESIN.
- IDENTIFICATION OF ORTHO AND PARA PHENOLIC CARBON UNREACTED SITES.
- HETEROSCALAR CORRELATION (HETCOR) TO LINK CARBONS TO PROTONS IS IN ANALYSIS.
- DOUBLE QUANTUM FILTERED CORRELATED SPECTROSCOPY (2D COSY) TO LINK PROTONS IS IN ANALYSIS.

A. J. Day 11 Nov 1991

APPENDIX D

RICK McINTYRE

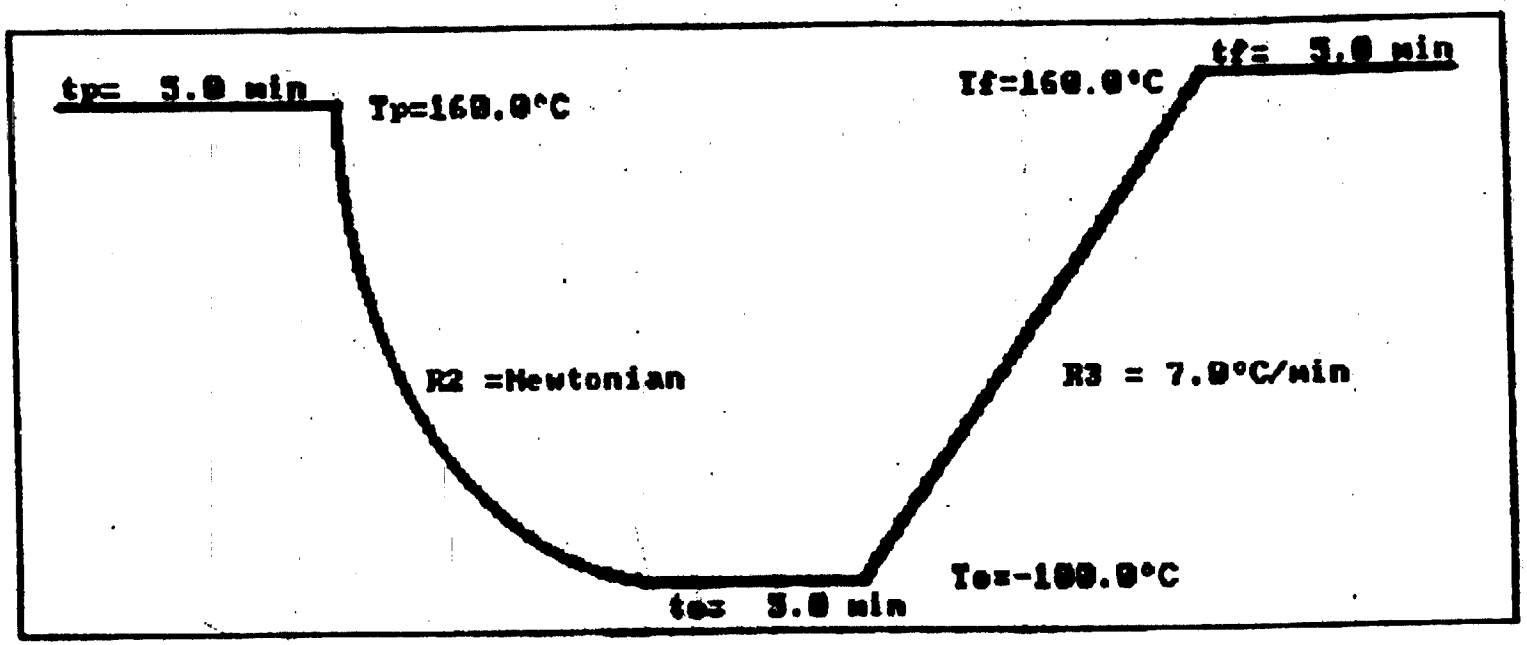
Information Available from TSC/RMA

* Degree of Cure
* Determination of Tg
* Influence of Thermal History
* Interpenetration of Phases
* Effects of Annealing
* Aging Studies
* Effects of Processing
* Determine Interfaces
* Information on Thermokinetic Functions

TSC Experiment

Anneal | Polarize | Freeze | Depolarize Experiment | Special

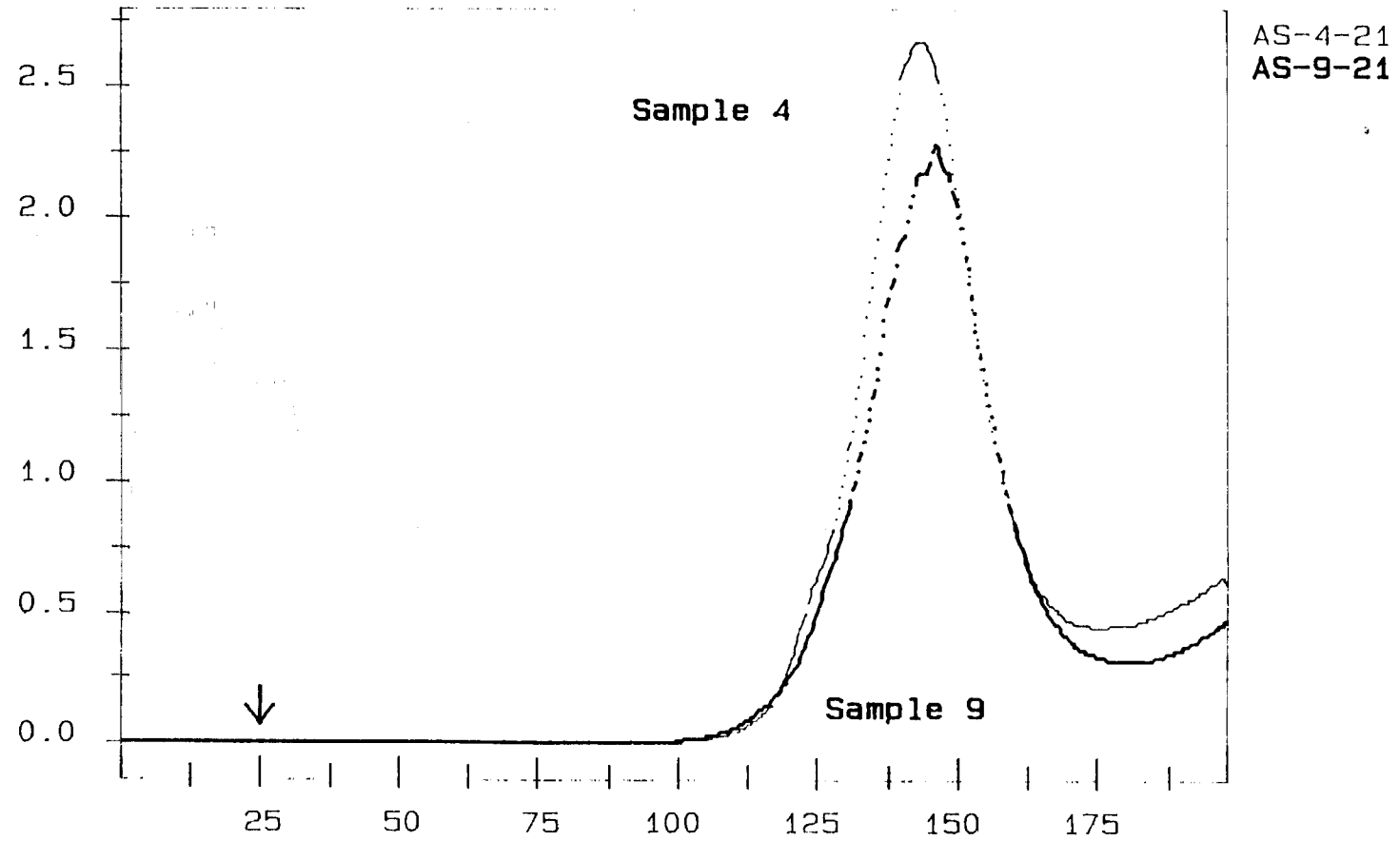
Standard TSC



Anneal OFF Field = 50.0 V/mm
Experiment Name: TSC Last Updated: 06/03/1991 Subdirectory:

PHENOLIC RESIN PELLETS
RAW MATERIAL EVALUATION

VARIATION IN MOL WEIGHT

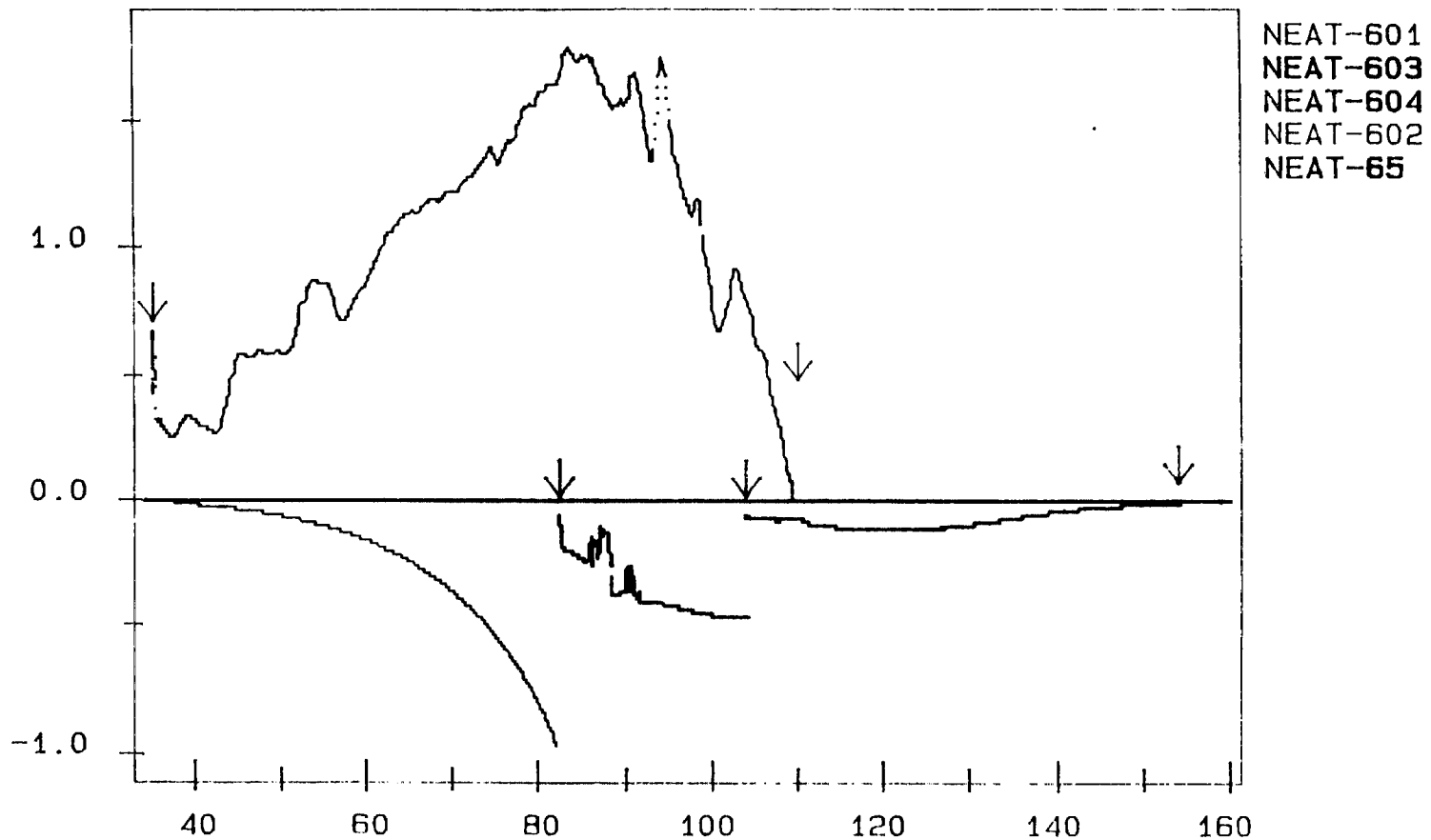


Nasa borden sc1008

File: NEAT-65.TSC

Current

Amps x 1E-09



NASA BORDEN SC 1008

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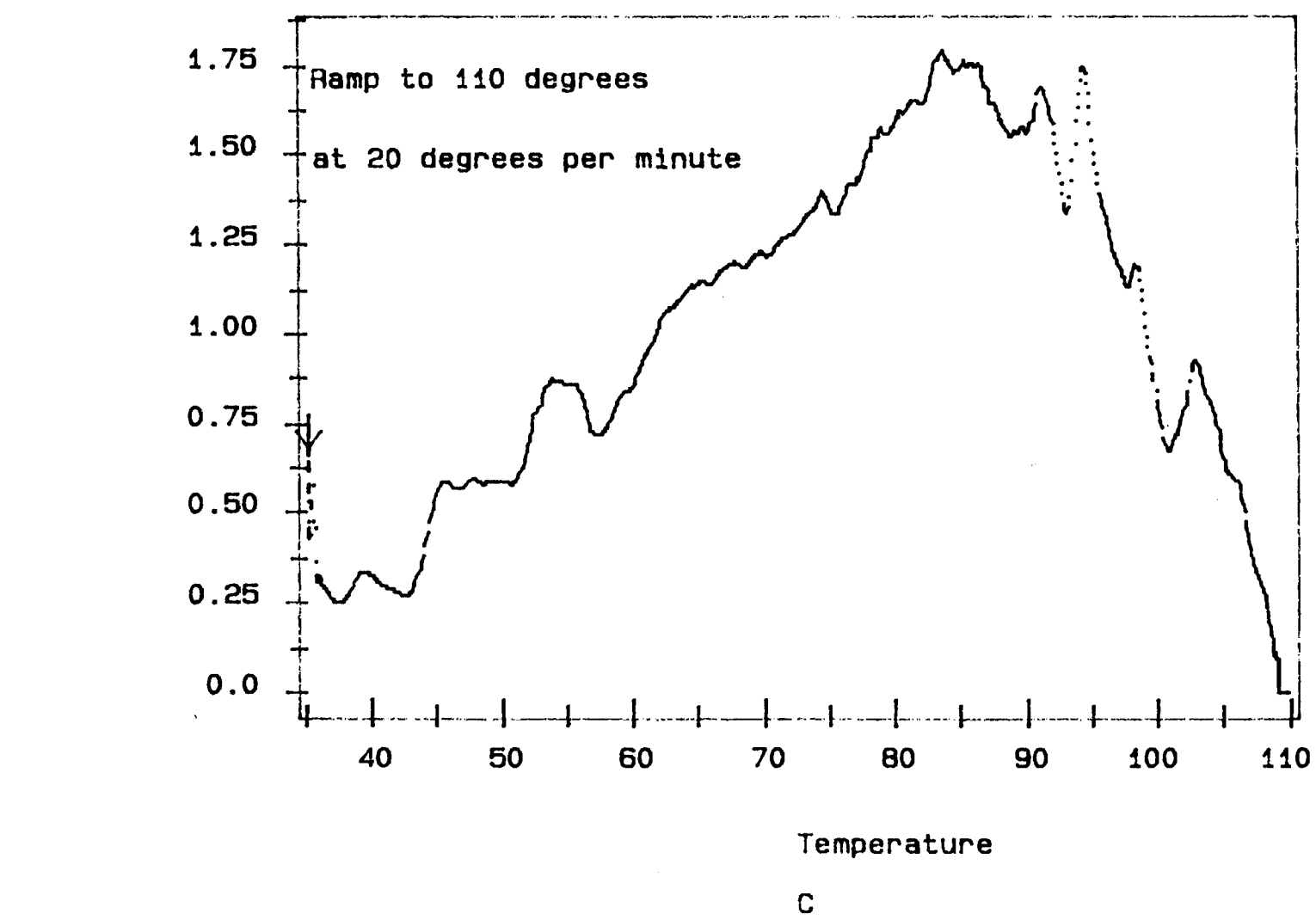
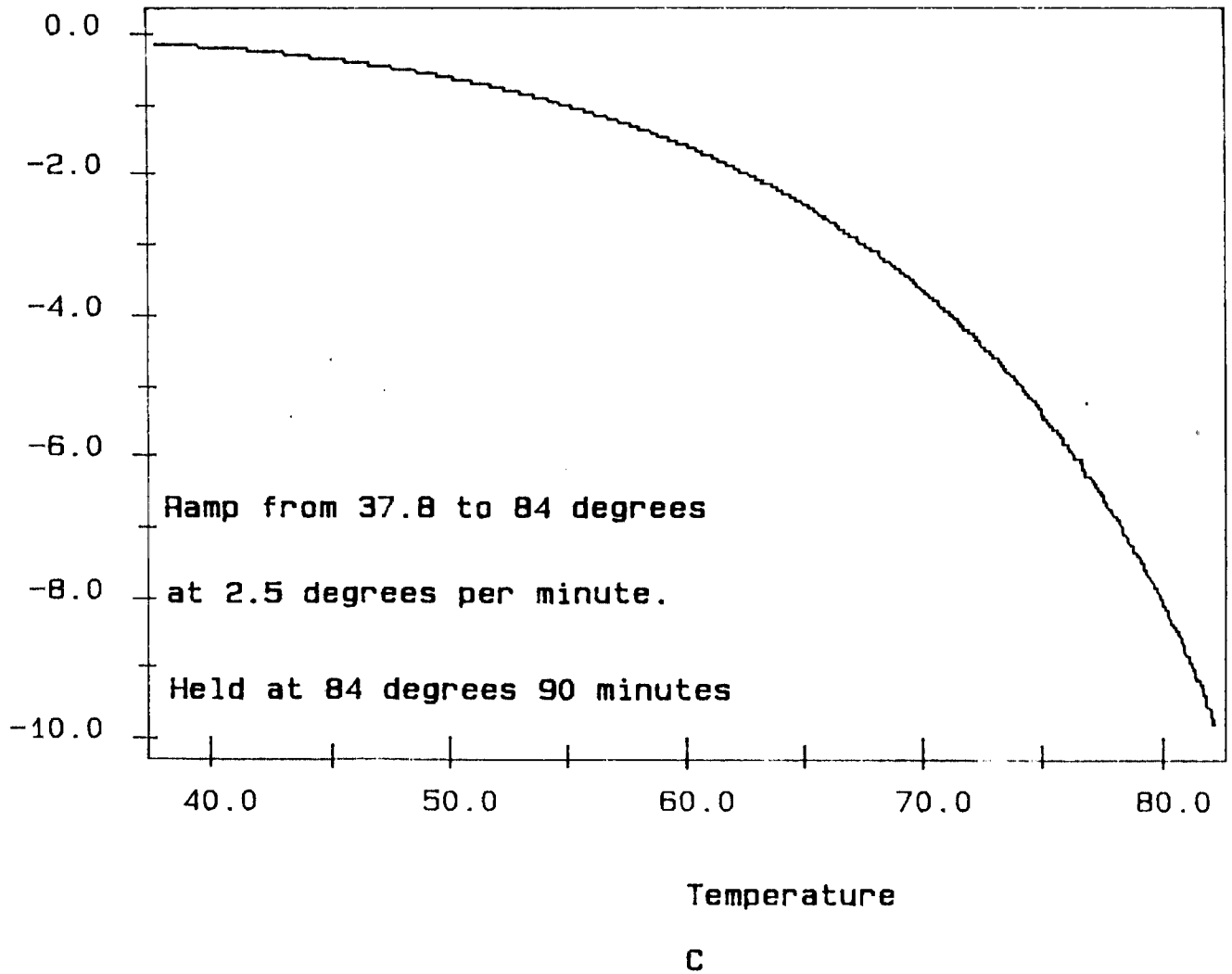


NASA BORDEN SC 1008

File: NEAT-602.TSC



NASA BORDEN SC 1008

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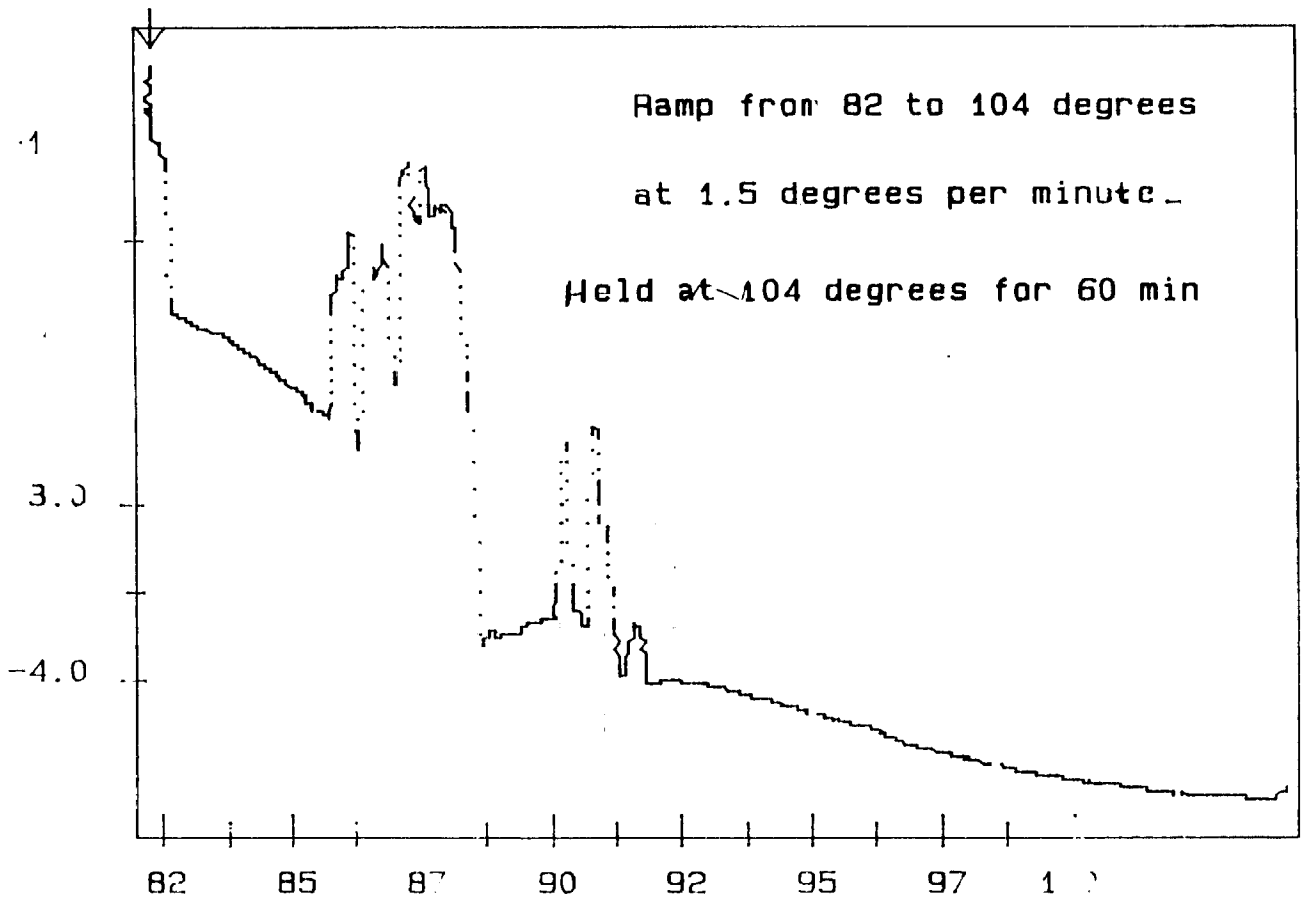
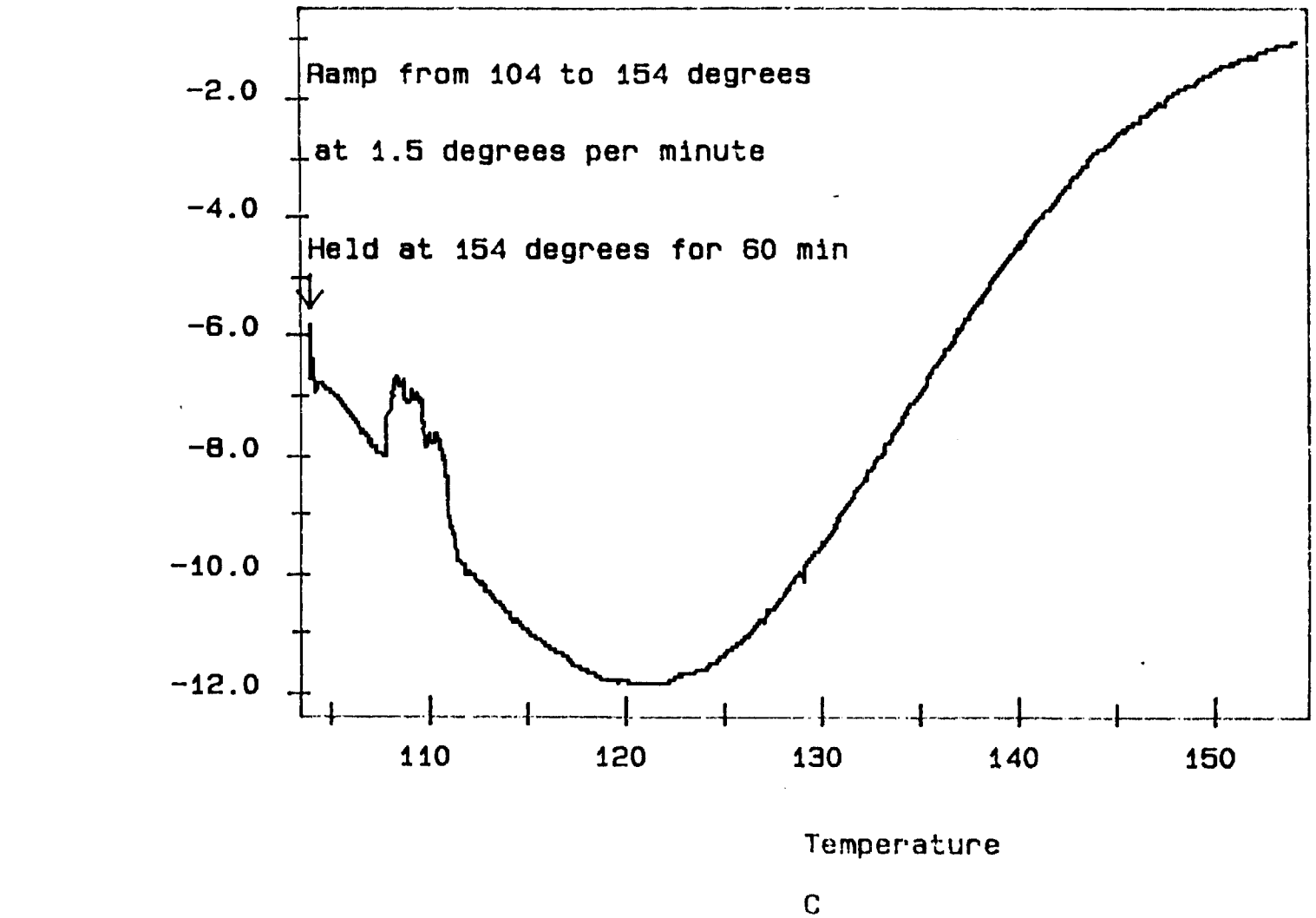


NASA BORDEN SC 1008

File: NEAT-604.TSC



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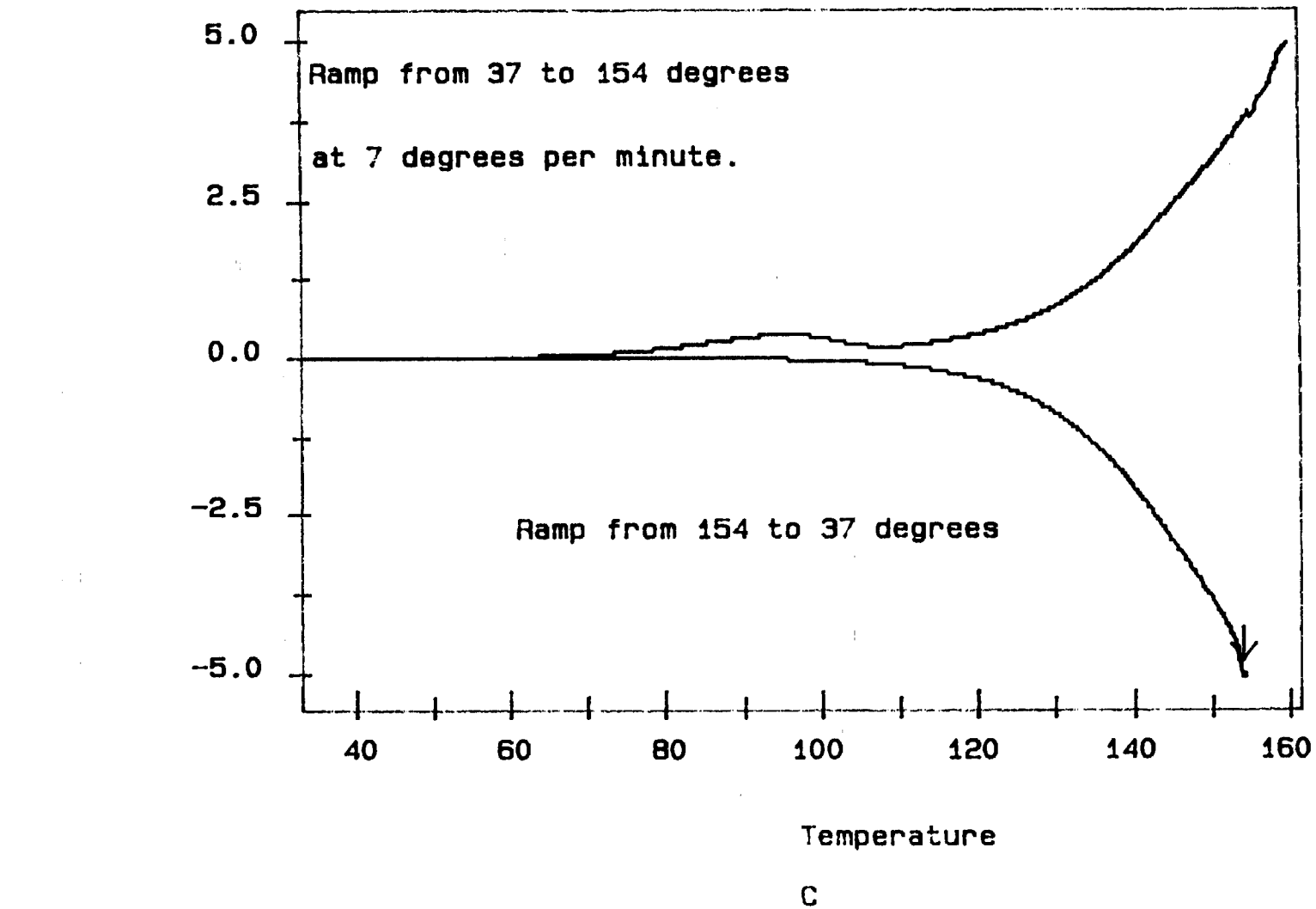
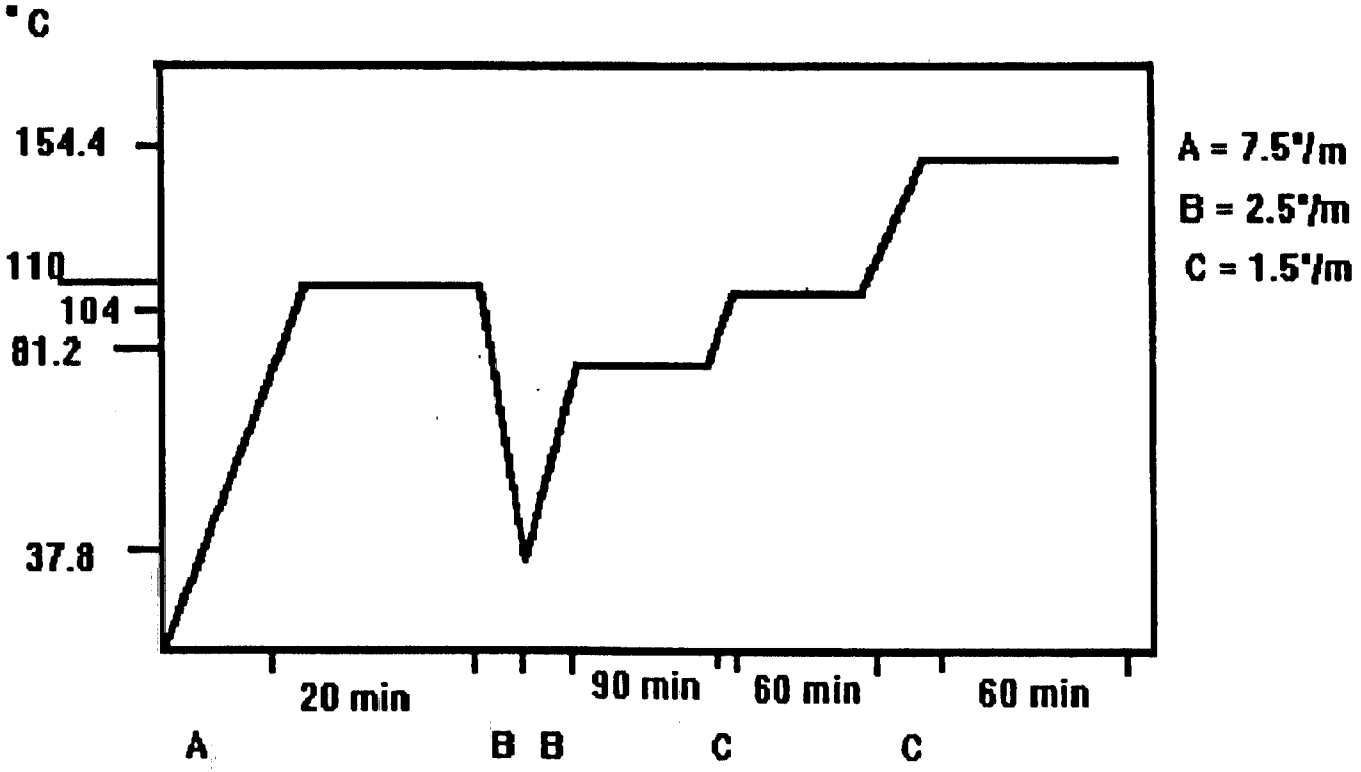
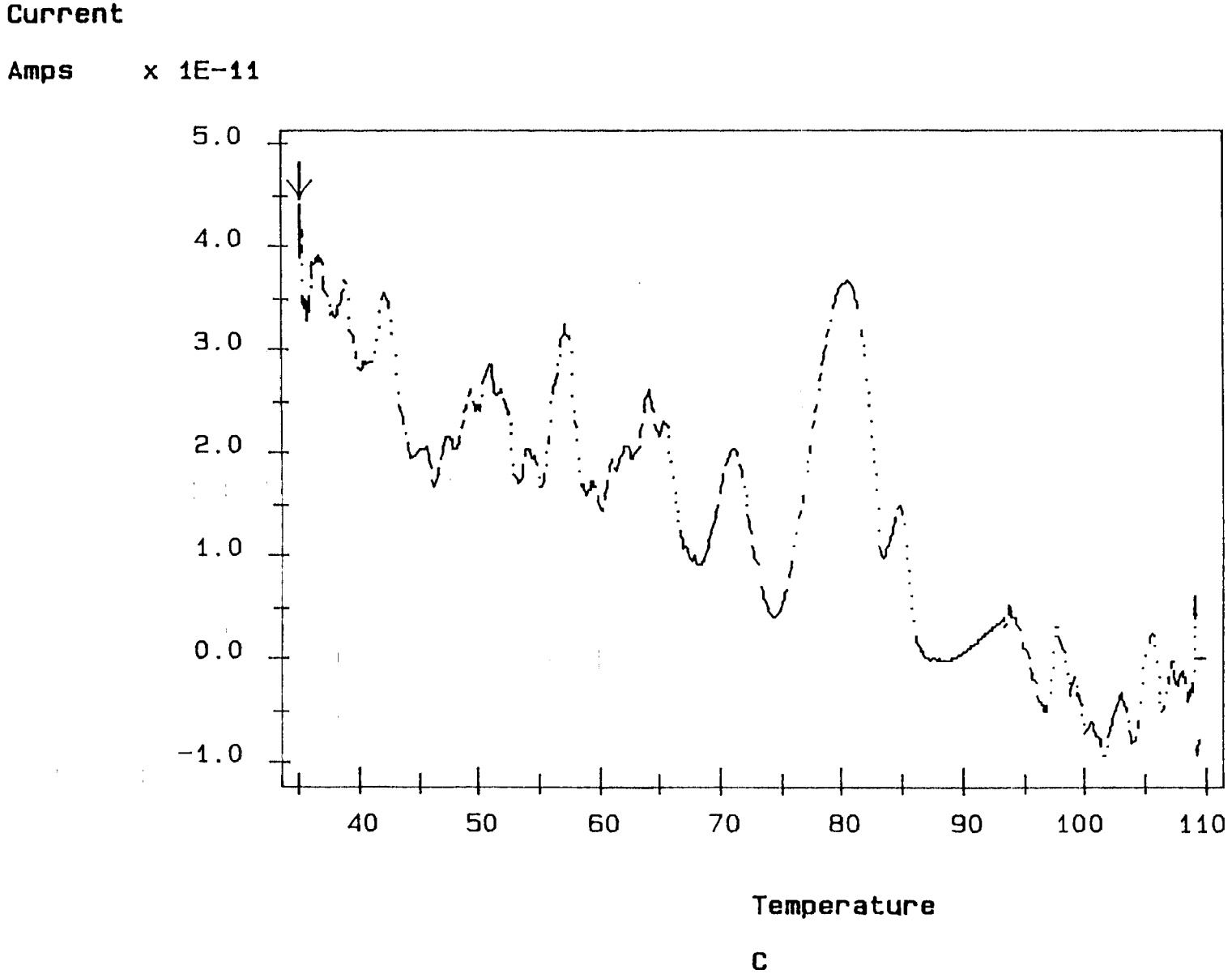


CURE CYCLE PROGRAM FOR PHENOLIC RESINS



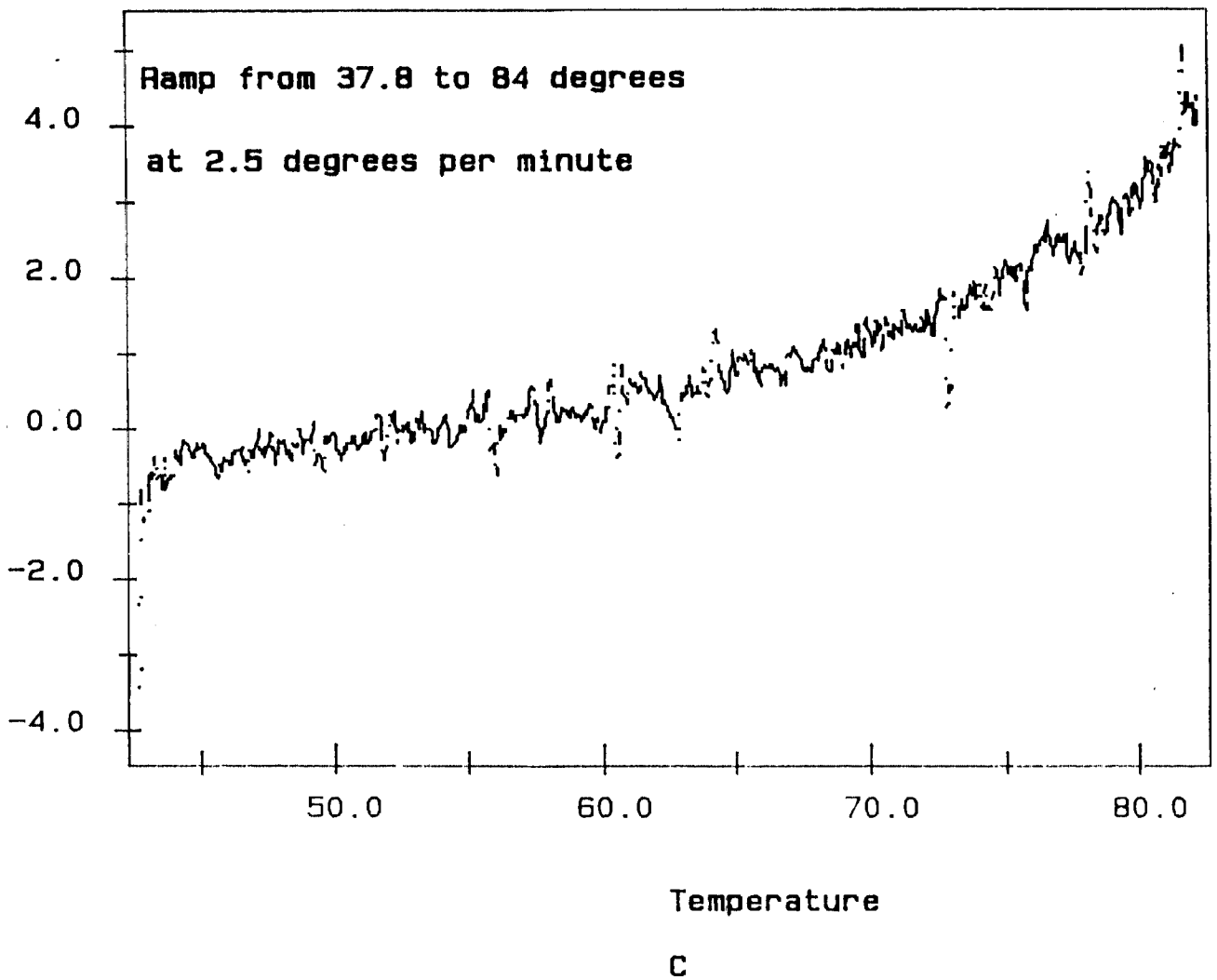
Nasa mx4926


Current
Amps x 1E-11
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
40
50
60
70
80
90
100
110
Temperature
C

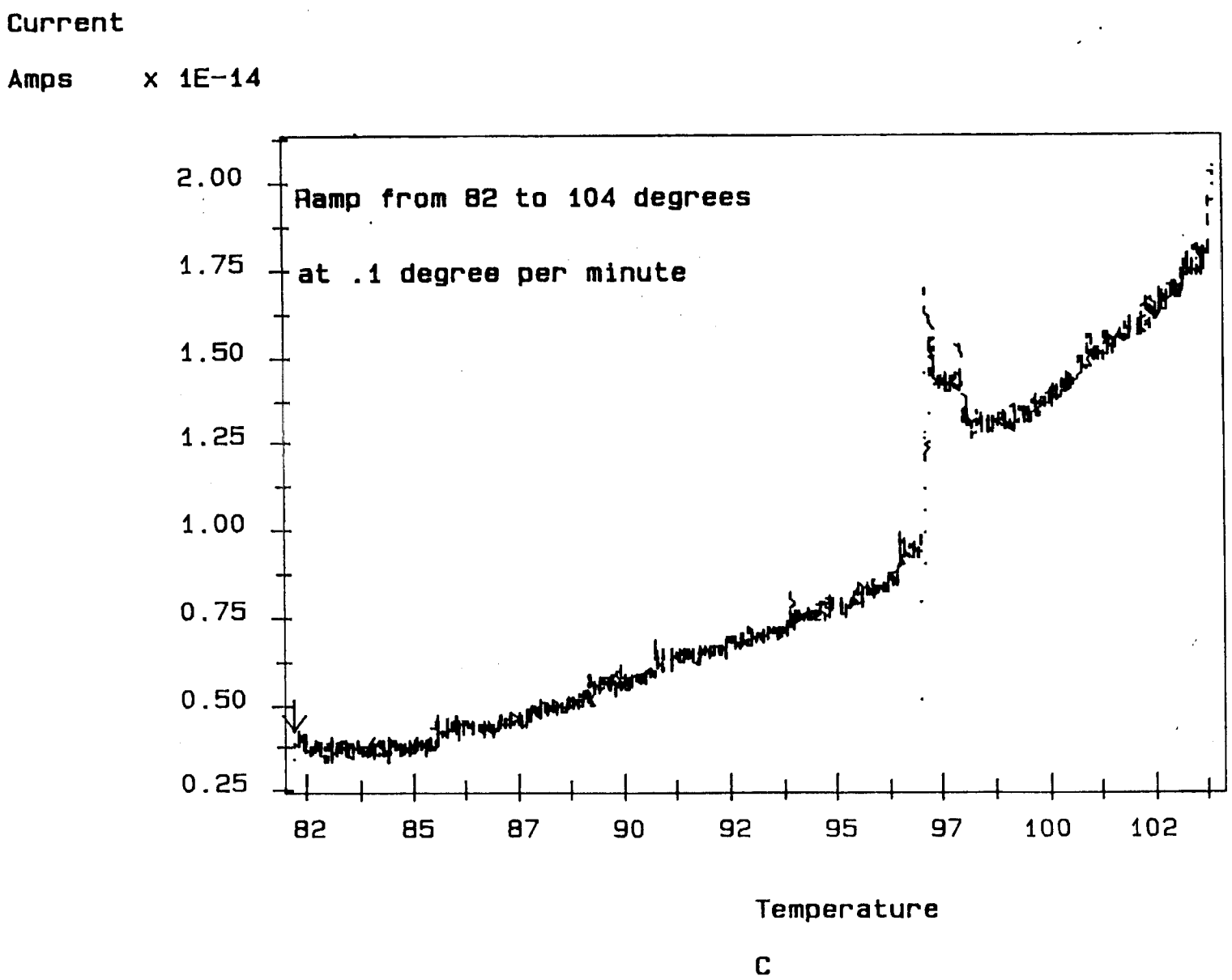
Nasa mx4926

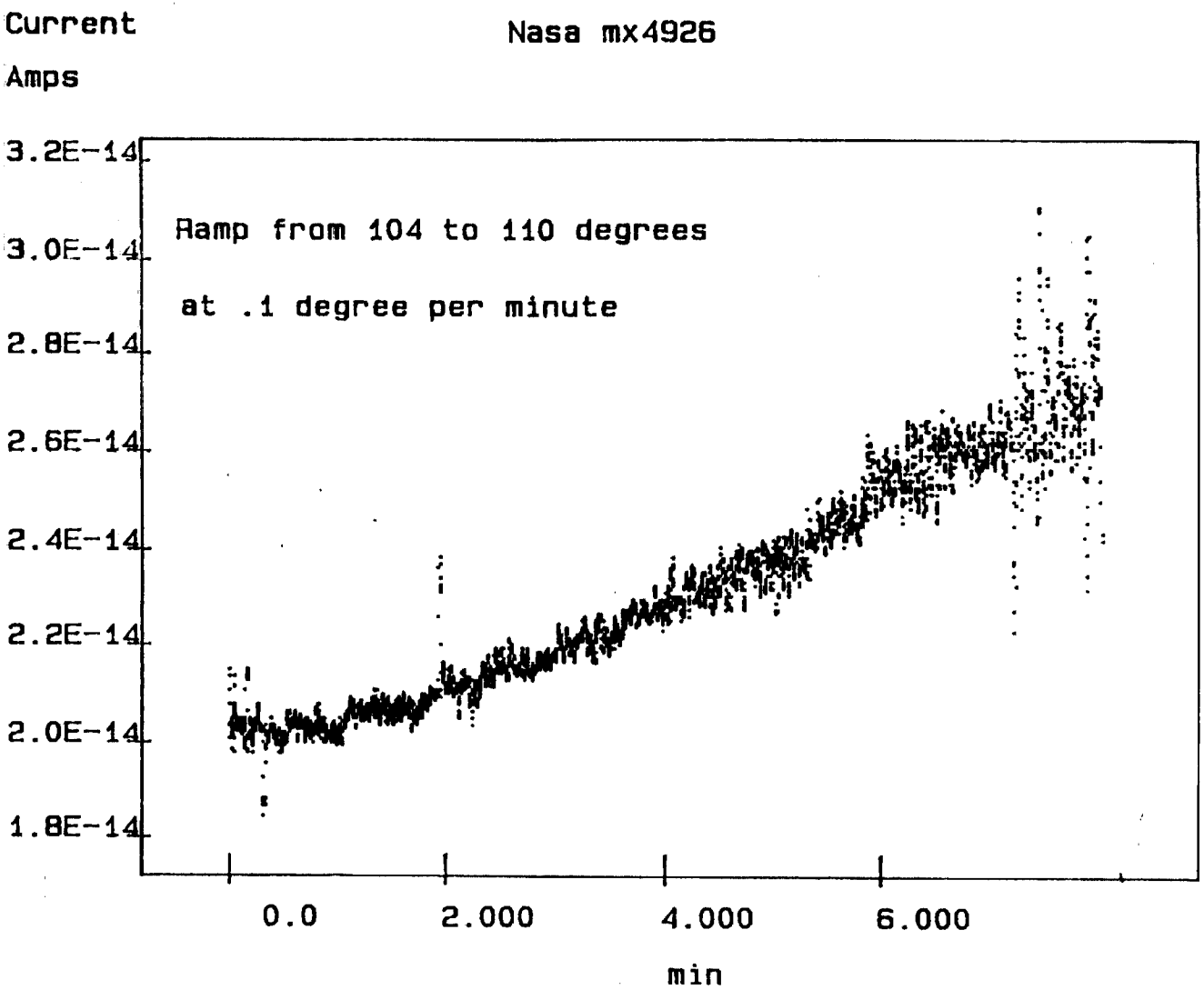
Current

Amps x 1E-15

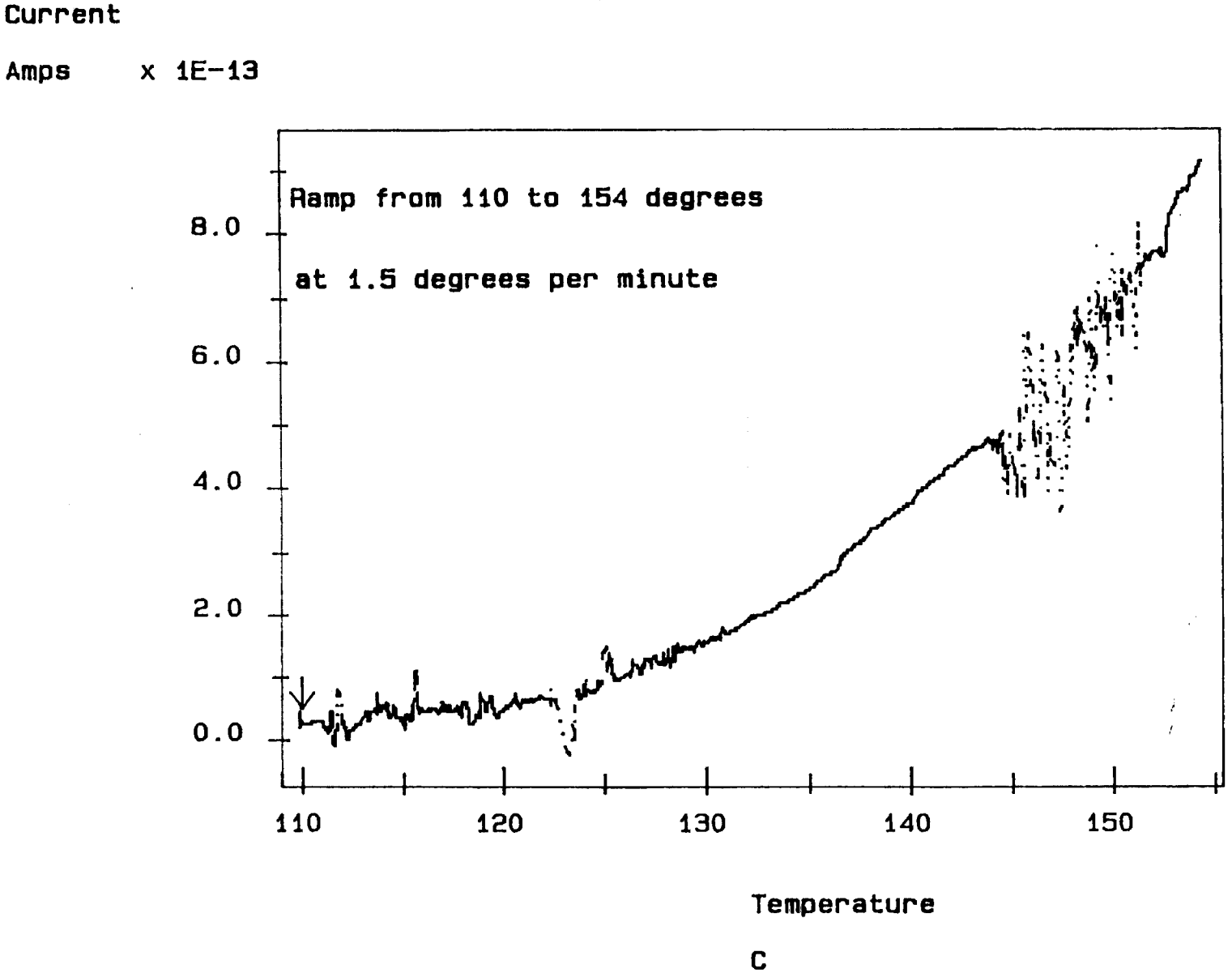


Nasa mx4926


Current
Amps x 1E-14
2.00
1.75
1.50
1.25
1.00
0.75
0.50
0.25
Ramp from 82 to 104 degrees
at .1 degree per minute
82
85
87
90
92
95
97
100
102
Temperature
C


Current
Amps
Nasa mx4926
Ramp from 104 to 110 degrees
at .1 degree per minute
3.2E-14
3.0E-14
2.8E-14
2.6E-14
2.4E-14
2.2E-14
2.0E-14
1.8E-14
0.0
2.000
4.000
6.000
min

Nasa mx4926


Current
Amps x 1E-13
Ramp from 110 to 154 degrees
at 1.5 degrees per minute
8.0
6.0
4.0
2.0
0.0
110
120
130
140
150
Temperature
C

APPENDIX E

JIM THOMAS

FIBERITE'S MX-4926 ABLATIVE MATERIAL

1. MATERIAL SUPPLIERS

   - AVTEX AND NARC RAYON YARN
   - HIGHLAND AND MILLIKEN WOVEN YARN
   - POLYCARBON, HITCO AND AMOCO CARBONIZED CLOTH
   - BORDEN'S SC-1008 RESIN

2. TEN COMBINATIONS

PRODUCT NO.	CODE
- MX-4926	AHP
- MX-4926	AHHI
- MX-4926	AHAM
- MX-4926	AMP
- MX-4926	AMHI
- MX-4926	AMAM
- MX-4926	NHP
- MX-4926	NHHI
- MX-4926	NMP
- MX-4926	NMHI

FIBERITE'S MX-4926 ABLATIVE MATERIAL

1. TEN COMBINATIONS

PRODUCT NO.	CODE
- MX-4926	A
- MX-4926	B
- MX-4926	C
- MX-4926	D
- MX-4926	E
- MX-4926	F
- MX-4926	G
- MX-4926	H
- MX-4926	I
- MX-4926	J

Advanced Materials

Fiberite is a business unit of ICI Composites Inc
FIBERITE
501 West Third Street
Winona, Minnesota 55987
(507) 454-3611
Fax: (507) 454-5105

THIOKOL CORPORATION
SPACE OPERATIONS
PO BOX 707
BRIGHAM CITY UT 84302-0707 USA

CERTIFICATION

ATTENTION: DALLAN DAY

Date: August 06, 1991

Product Purchased:	MX 4926-B.G.
Date Shipped:	08/06/91
Quantity Shipped (LB):	7180.42
Your Purchase Order No.:	OSDO25,DR#402837 DATED 07/10/91 AND DWD LET
Fiberite Order Number:	1597 #4410-FY92-027 DATED 07/30
Specification:	STWS-3279 REV.A SCN 3C,4B
Lot Number:	10297

We certify that this Fiberite product ordered on the above purchase order has been tested in accordance with the applicable specification procedures and found to possess the following properties, therefore meeting the requirements of your requested specification.

PDL 4997 REV. 15
FIBERITE LOT NO.: 10297
DATE OF ACCEPTANCE TESTING:06-26-91
RESIN CONFORMS TO:
RESIN DESIGNATION:
FABRIC CONFORMS TO:
FABRIC DESIGNATION:
STORAGE LIFE:

REF:PACKING LIST NO.:

W91-0553

STOCK/LOT NO.: 4997-1141
DATE OF MANUFACTURE: 06-21-91
CARBON ASSAY OF RESIN FILLER: 90% MIN.
MIL-R-9299C, GRADE A
BORDEN SC-1008
STW4-3184 REV.B SCN 3,4
POLYCARBON CSA
6 MONTHS AFTER DATE OF MANUFACTURE
@ 50 DEG. F MAX.
20008248

Dawn Thurlby
Representative, Quality

ICI Advanced Materials

Fiberite is a business unit of ICI Composites Inc.
FIBERITE
501 West Third Street
Winona, Minnesota 55987
(507) 454-3611
Fax: (507) 454-5105

KAISER AEROTECH
880 DOOLITTLE DRIVE
PO BOX 1678
SAN LEANDRO CA 94577-0801 USA

CERTIFICATION

ATTENTION: CAL MC CULLOUGH

Date: May 15, 1991

Product Purchased:	MX 4926 B.T.
Date Shipped:	05/16/91
Quantity Shipped (LB):	1122.78
Your Purchase Order No.:	1995
Fiberite Write-up#:	647,650,653
Specification:	S123188 N/C TYPE I W/EXCEPTION
Lot Number:	10181

We certify that this Fiberite product ordered on the above purchase order has been tested in accordance with the applicable specification procedures and found to possess the following properties, therefore meeting the requirements of your requested specification.

Sublot	VOLATILE CONTENT %	% RESIN FLOW @ 150 PSI	FABRIC CONTENT %	FILLER CONTENT %	RESIN SOLIDS %
Spec. Limits: Minimum -	3.5	8.0	47.0	5.0	32.0
Maximum -	5.0	18.0	63.0	16.0	37.0
001A	3.9	10.9	54.6	11.2	34.2
HEAD	4.3	10.1	53.8	12.3	33.9
	4.6	11.8	55.4	11.6	32.9
AVERAGE	4.3	10.9	54.6	11.7	33.7
[illegible]	[illegible]	[illegible].8	58.6	8.9	32.5
TAIL	4.2	[illegible]	56.6	10.3	33.1
	4.3	13.[illegible]	57.8	8.9	33.3
AVERAGE	4.2	12.3	57.7	9.2	33.1

BIAS TAPE SIZE:	SEE ATTACHED SHEET.
DATE OF MANUFACTURE:	04-16-91
DATE OF ACCEPTANCE TESTING:	04-22-91
CARBON ASSAY OF RESIN FILLER:	90% MIN.
REINFORCEMENT CONFORMS TO:	S123187 REV. N/C
SPECTRUM NO.:	X-40329, PASS

STORAGE LIFE/CONDITIONS: 6 MONTHS FROM DATE OF MANUFACTURE @ 50 DEG.F MAX. WHEN STORED IN SEALED AND MOISTURE RESISTANT PACKAGING.
WORKMANSHIP CONFORMS TO: PARA. 3.7, PASS
VISUAL EXAMINATION CONFORMS TO: PARA. 3.4, 3.5.1, 3.6, AND SECTION 5
REF:PACKING LIST NO.:20006656,20006657,20006658

W91-0438

Dawn Thursley
Representative, Quality

APPENDIX F

DON BECKLEY

BPCHI GRADE CODE SYSTEM

RESIN SYSTEM	FAMILY	PREPREG (RESIN + REINF.
R 200-299	Elastomer	RM 2000-2999
R 300-399	Misc.	RM 3000-3999
R 400-499	Melamine	MM 4000-4999
F 500-599	Phenolic	FM 5000-5999
P 600-699	Polyester	PM 6000-6999
E 700-799	Epoxy	EM 7000-7999
S 800-899	Silicone	SM 8000-8999
V 900-999	Special	VM 9000-9999

(eg) F502 SC-1008
F508 91LD
F508T 91LD + Carbospheres + Elastomer + _____

USP 1-100 Misc. Chem., Req., Outside Reference

(eg) USP 27
USP 28 } Qualified Carbon Blacks
USP 29

M = Material, Fabric
F = Filament, Roving
T = Towable

(eg) FM = Phenolic Broadgoods, Tape or Molding Compound
FF = Phenolic Filament

(X) FM = Until BP & Customer Concur

APPENDIX G

GREG CROSE

SOURCES OF UNRELIABILITY
(Material Variability)

By:
J.G. Crose
PDA Engineering
2975 Red Hill Avenue
Costa Mesa, California 92626

November 14, 1991

Presented To:
SPIP Industry Advisory committee on
Carbon-Phenolic Constituent
and Composite Test Methodology

At:
Gencorp - Aerojet
Propuslion Division
Sacremento, California

SOURCES OF UNRELIABILITY
(Material Variability)

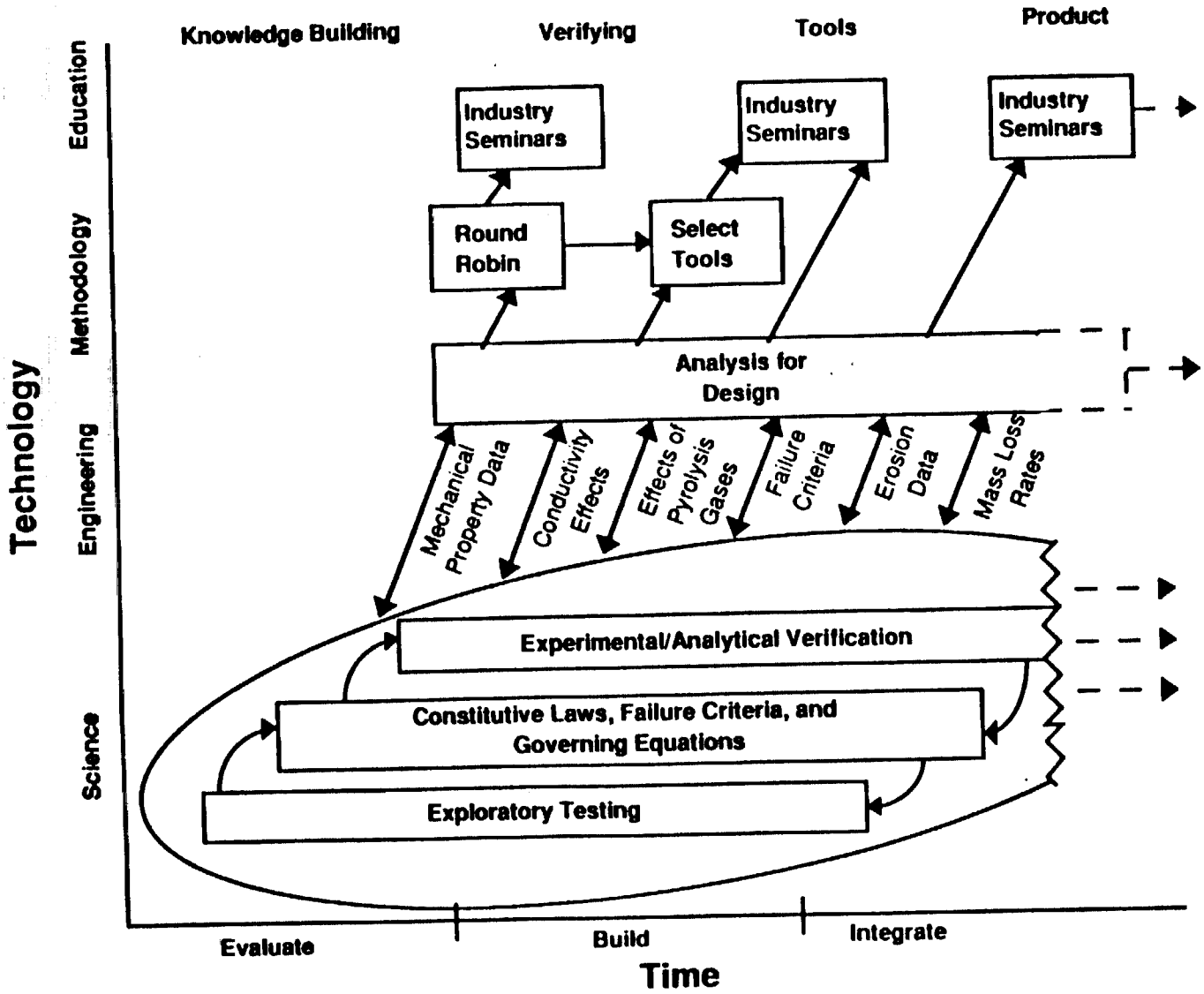
By:
J.G. Crose
PDA Engineering
2975 Red Hill Avenue
Costa Mesa, California 92626

November 14, 1991

Presented To:
SPIP Industry Advisory committee on
Carbon-Phenolic Constituent
and Composite Test Methodology

At:
Gencorp - Aerojet
Propuslion Division
Sacremento, California

MATERIAL CHARACTERIZATION & DESIGN ANALYSIS



SOURCES OF UNRELIABILITY
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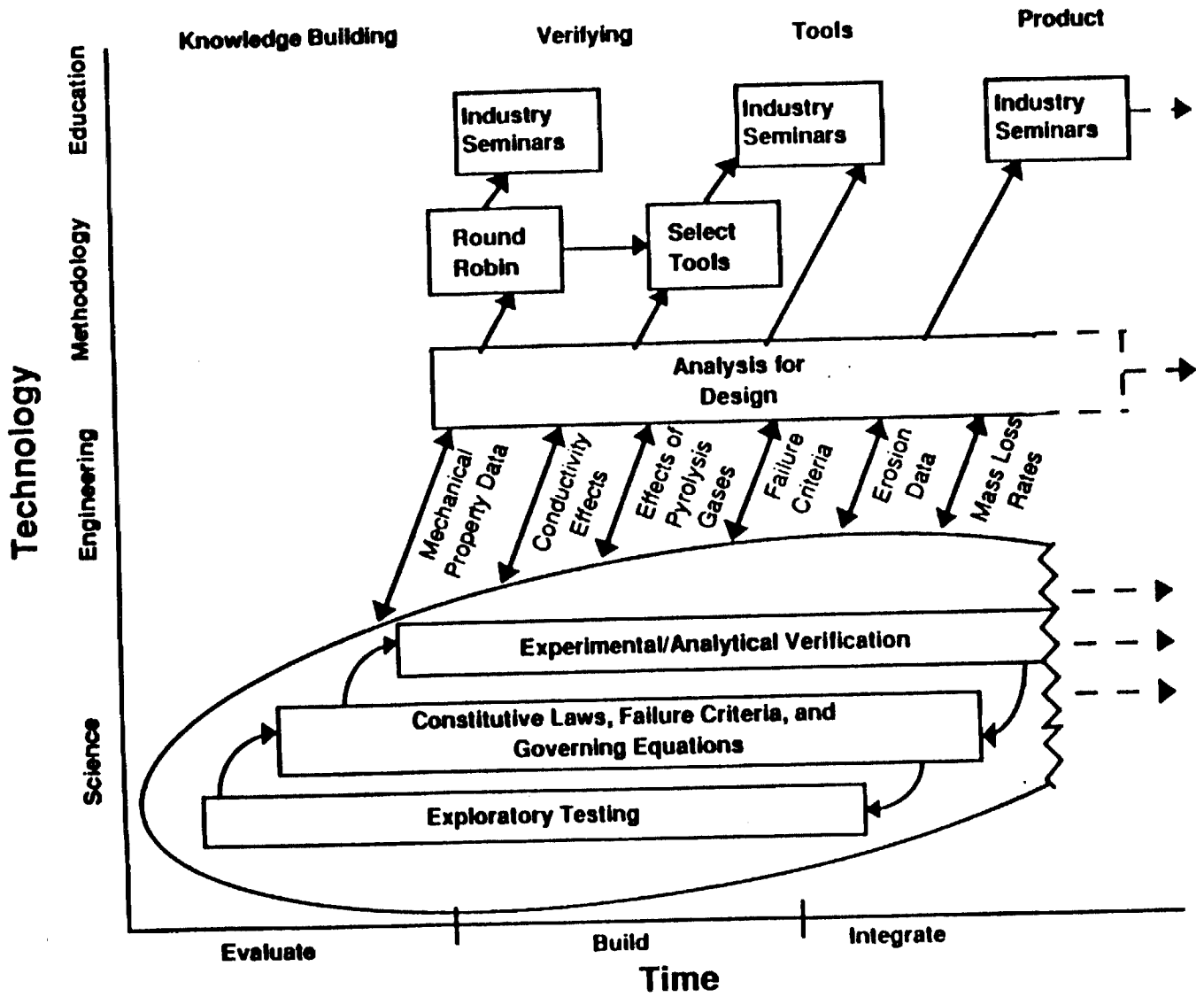
Carbon-Phenolic Constituent
and Composite Test Methodology

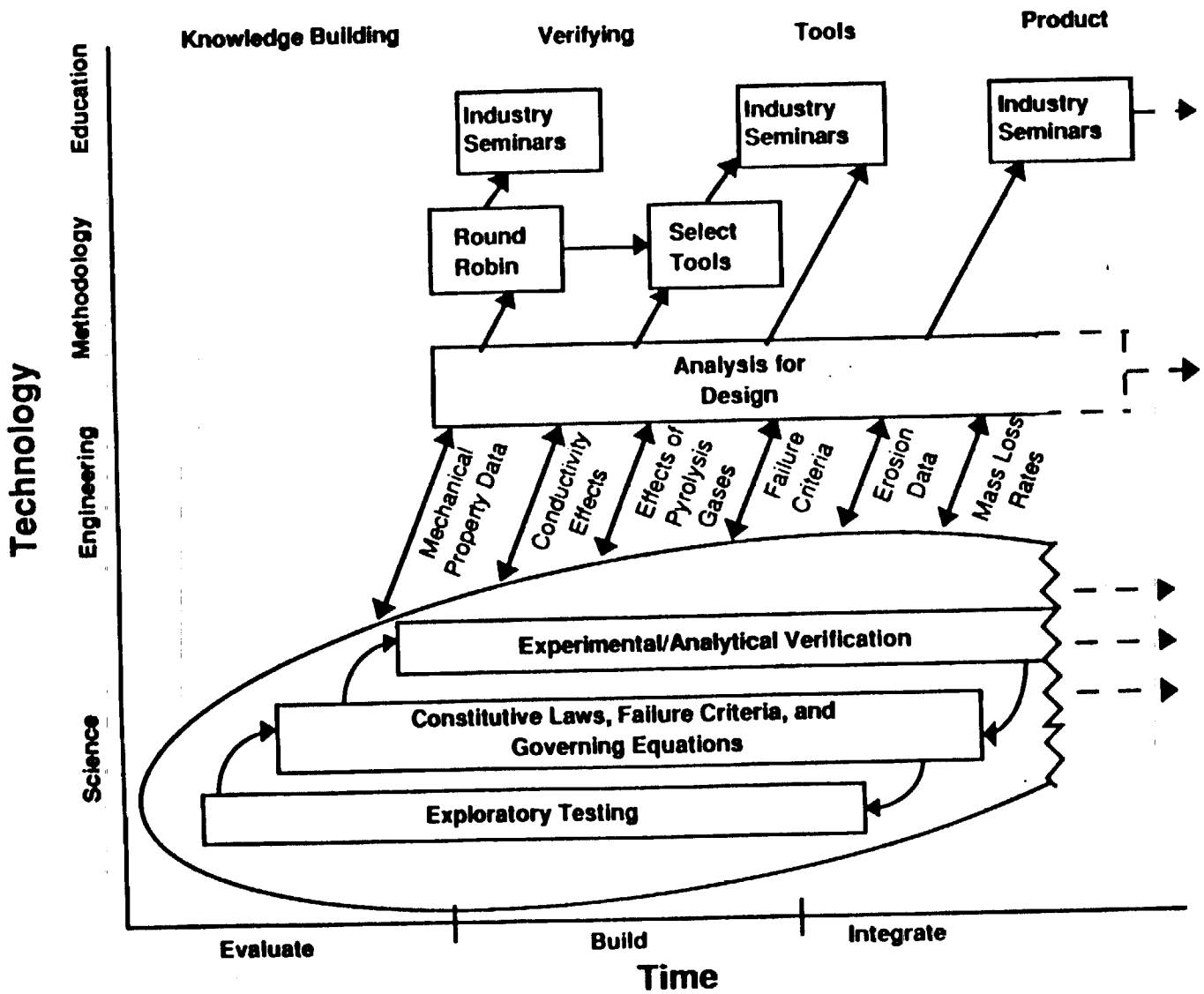
At:
Gencorp - Aerojet
Propuslion Division
Sacremento, California

MATERIAL CHARACTERIZATION & DESIGN ANALYSIS



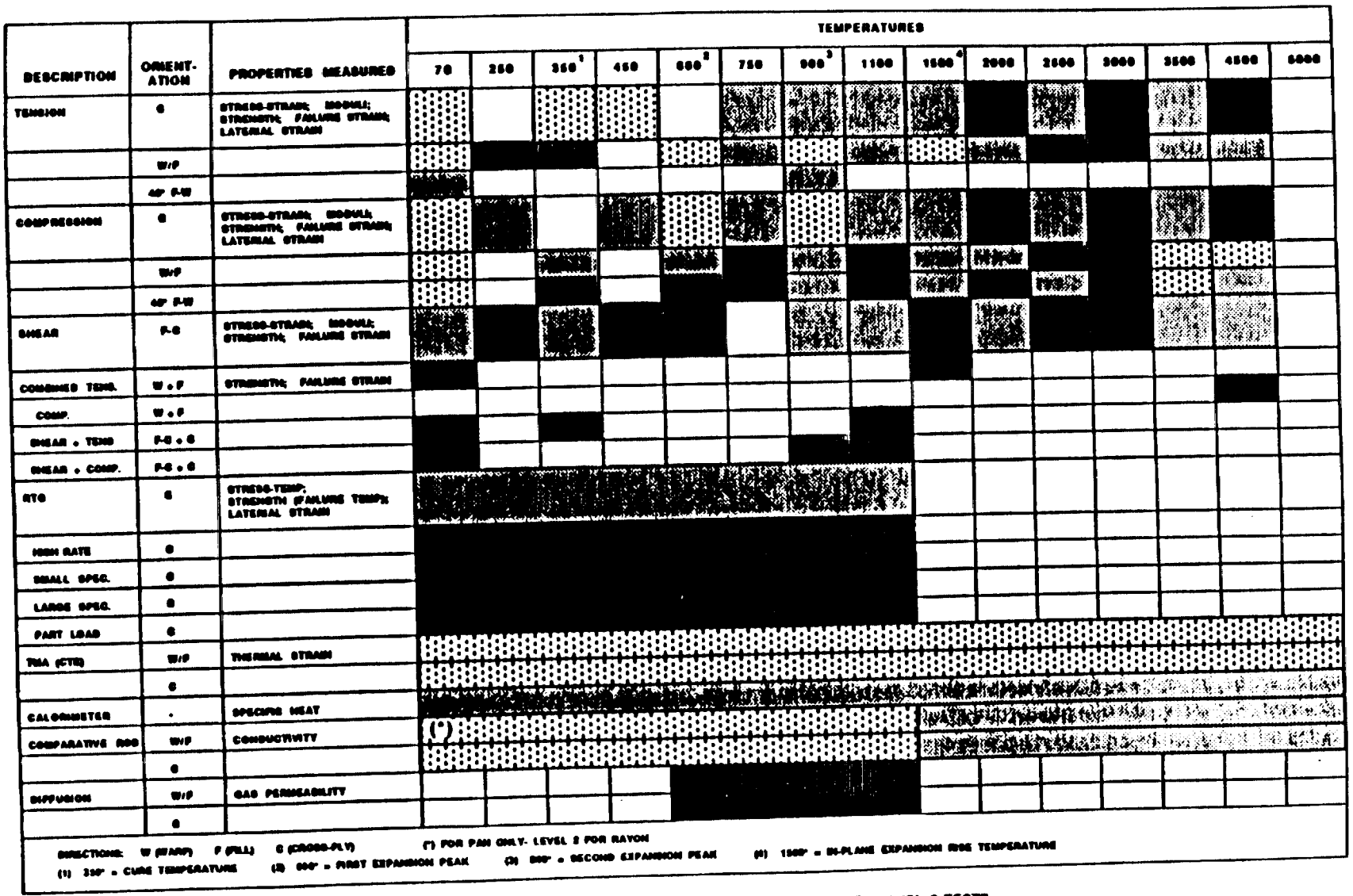
PDA ENGINEERING

MATERIAL CHARACTERIZATION & DESIGN ANALYSIS



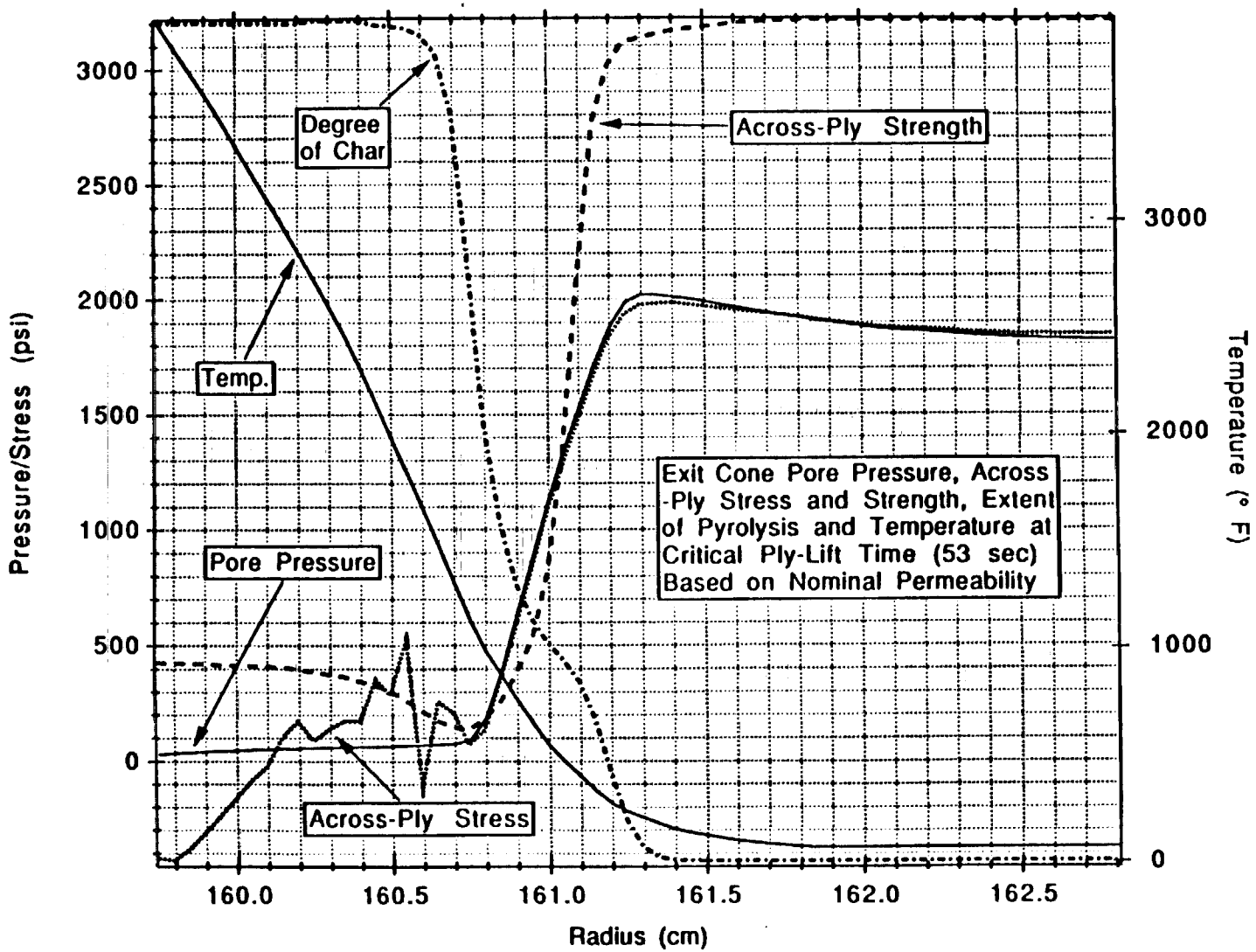
pdo ENGINEERING

DATA BASE DEVELOPMENT TESTS



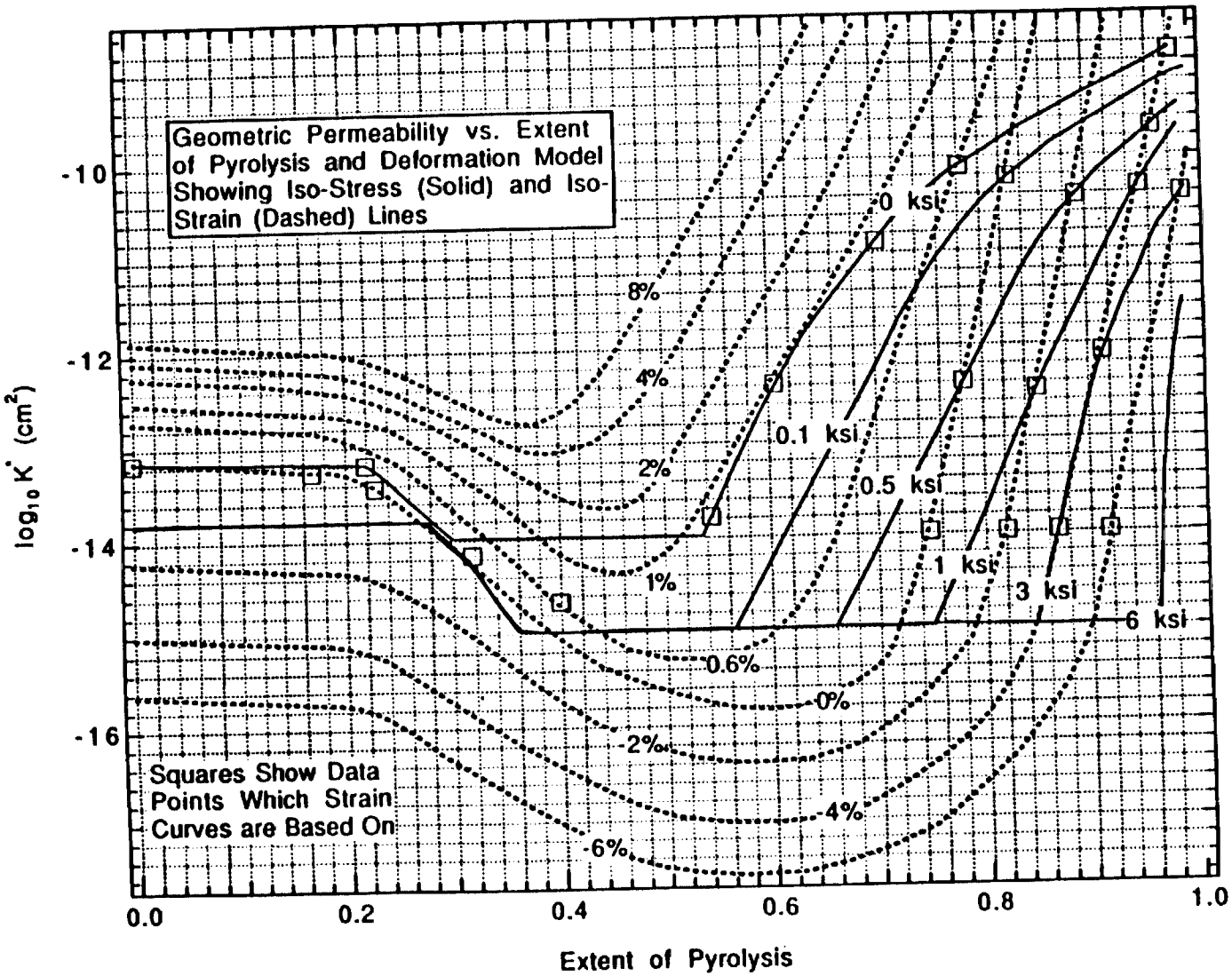
pda ENGINEERING

SUBTASKS 3.1.1.2 AND 3.1.2.1



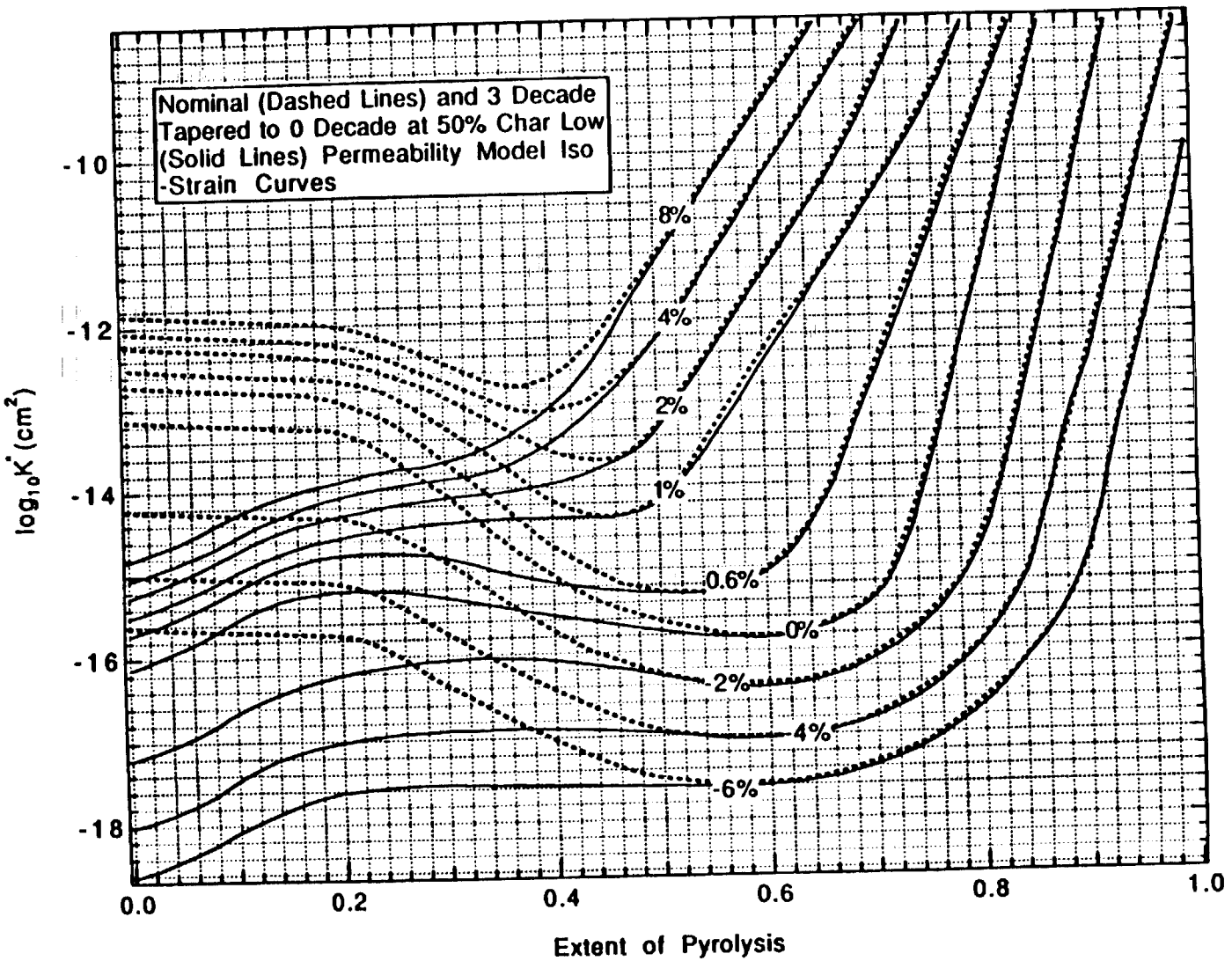
PDA ENGINEERING

SUBTASKS 3.1.1.2 AND 3.1.2.1



pda ENGINEERING

SUBTASKS 3.1.1.2 AND 3.1.2.1



PDA ENGINEERING

SPIP TASK 3.1 GOALS

- **Analysis Codes**
  - + Predict average response and standard deviation
  - + Achieve confidence in predictions

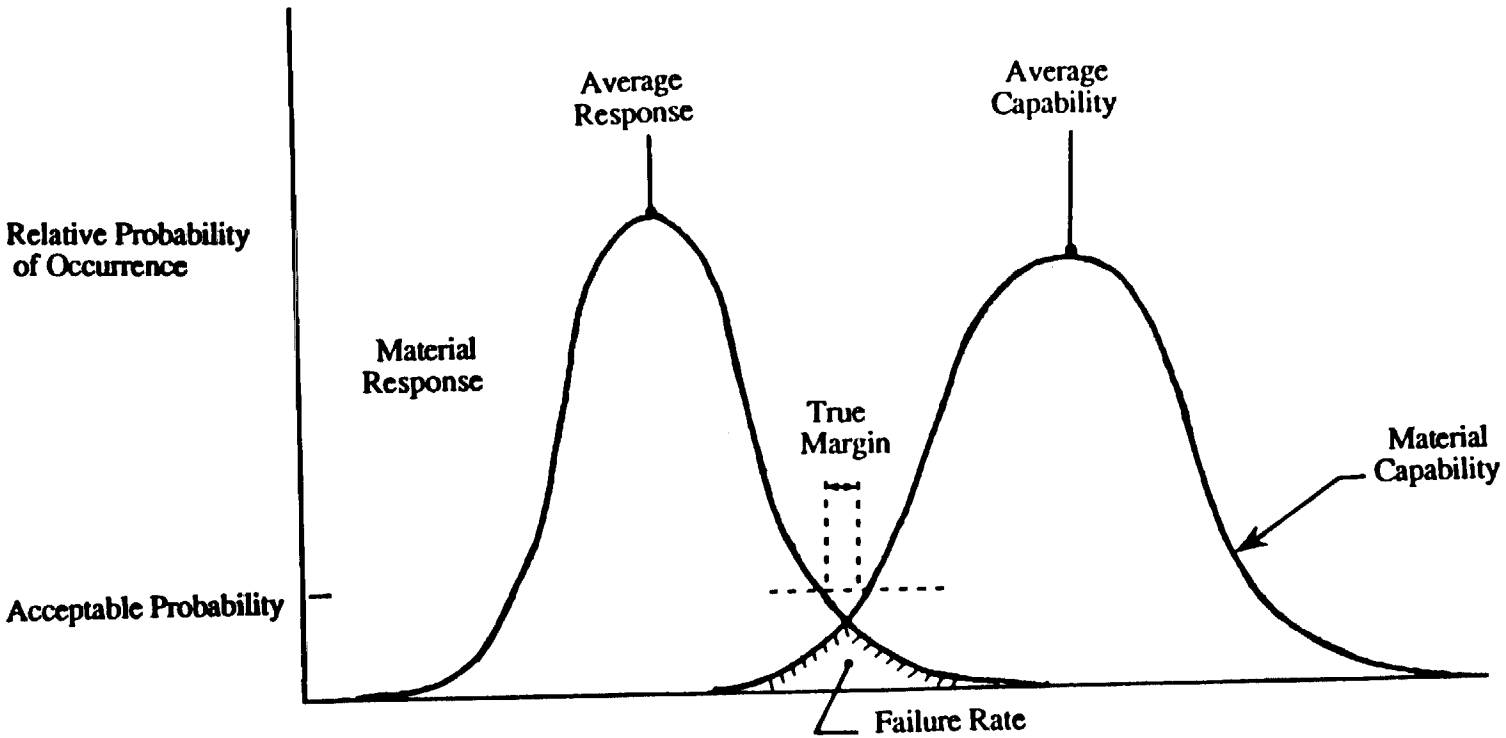
- **Failure Criteria**
  - + Predict average strength and standard deviation
  - + Achieve confidence in predictions

- **Application**
  - + Verify predicted response
  - + Verify calculated margins

} Task 3.3

PDA ENGINEERING

STATISTICAL REALITY OF FAILURE



FRACTURE ENERGY OR ?

PDA ENGINEERING

ROLE OF CONSTITUTIVE PROPERTY TESTING IN SYSTEM RELIABILITY

- Determine variability in all measurable attributes of constituents
- Relate constituent properties to performance
  - Intuition
  - Statistical Correlation
  - Theory
- Establish specifications
- Insure product uniformity by enforcing specifications

PDA ENGINEERING

SPIP TASK 3.1 AND 3.2 RELATED AREAS

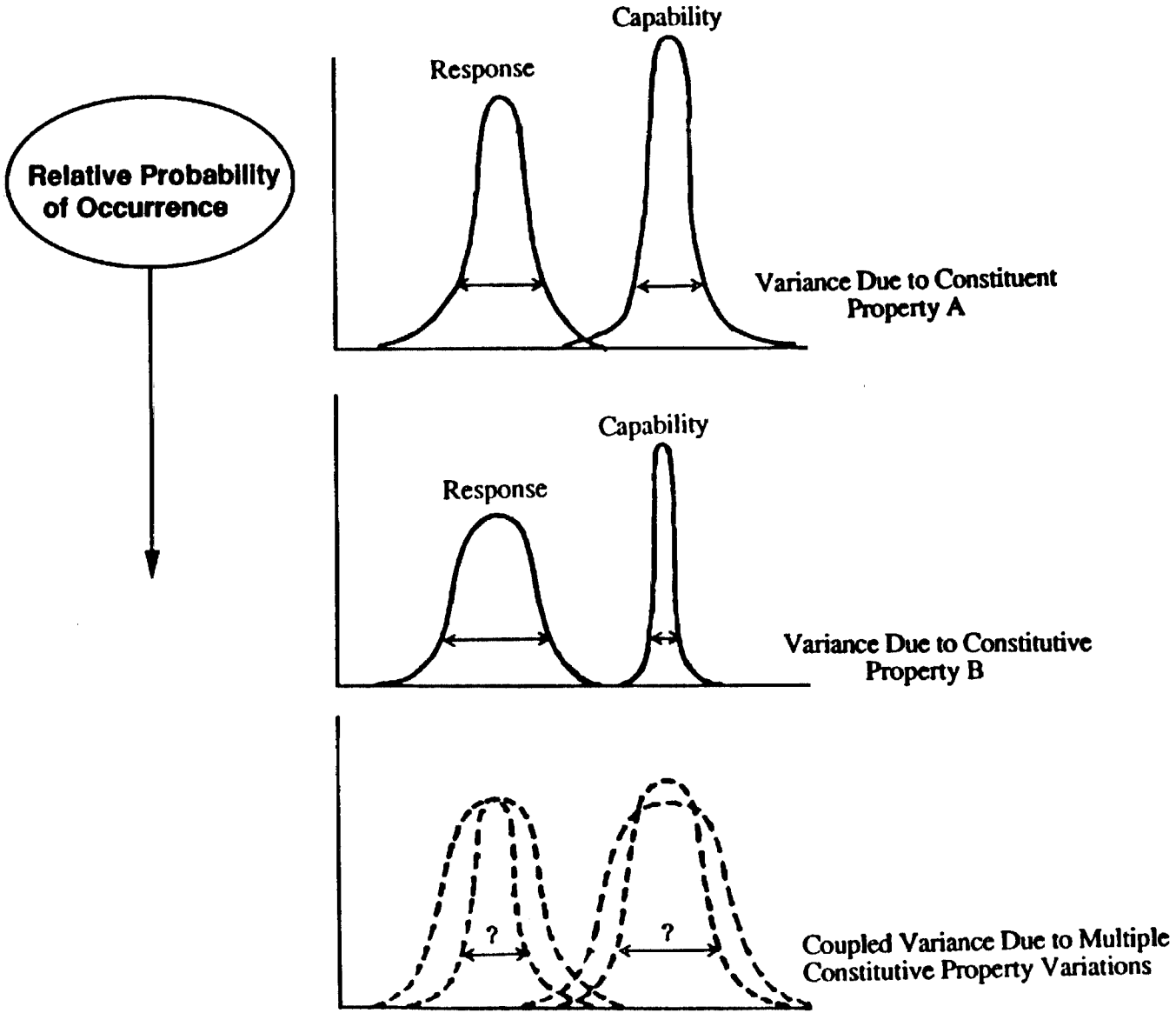
- Sources of Variability
  - Product Uniformity - Constitutive Test Methods/Data
  - Constituent Test Data Variability - Statistical Data Base

- Data
  - Establish relational data base
  - Relate constituent test results to composite performance

- Physics
  - Observe relationships for physical insight

PDA ENGINEERING

INFLUENCE OF CONSTITUENT VARIATIONS ON RELIABILITY

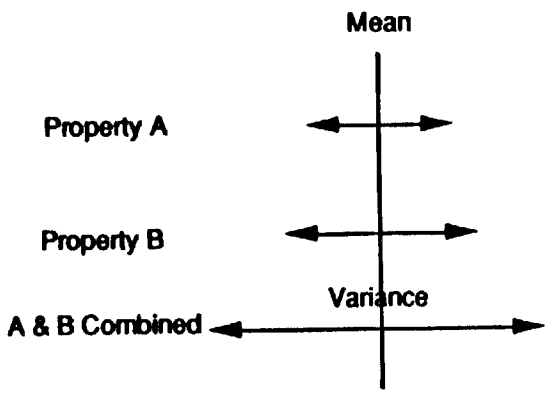


FRACTURE ENERGY

pda ENGINEERING

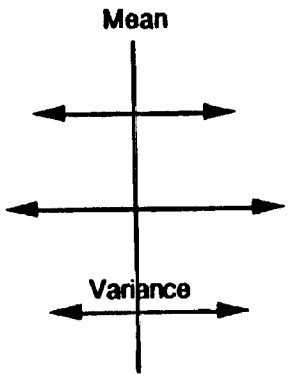
VARIABLE DEPENDENCE

Independent Variables



Variance Tends to be Additive

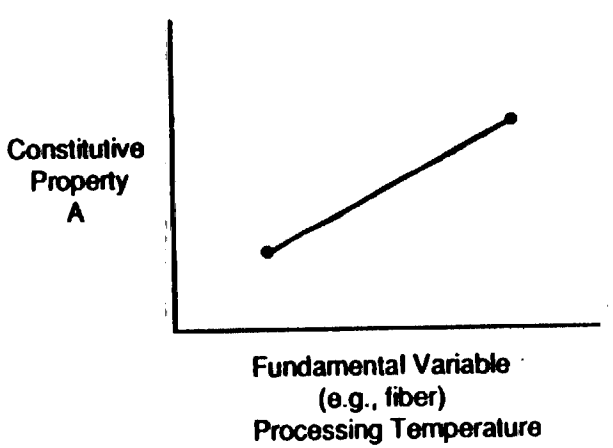
Dependent Variables

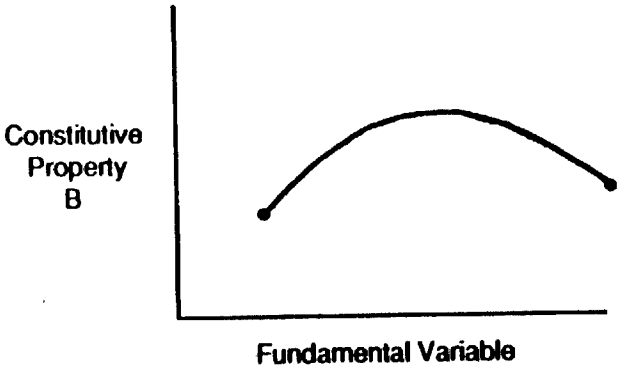


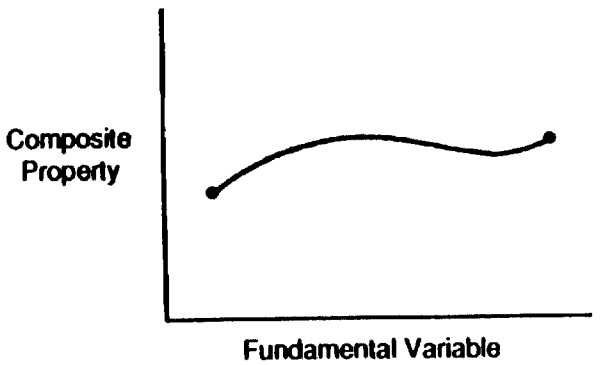
Variance May be Smaller or Larger Than Individuals

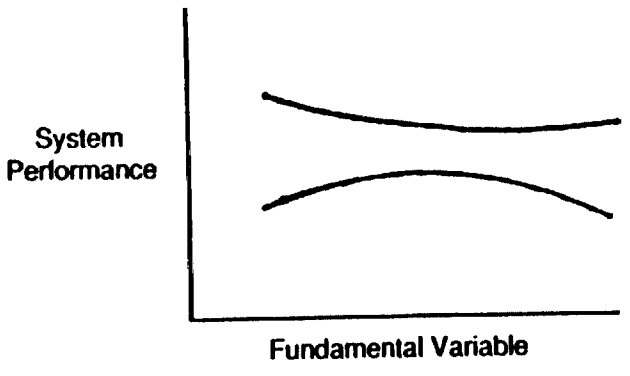
pdo ENGINEERING

FUNDAMENTAL VARIABLES



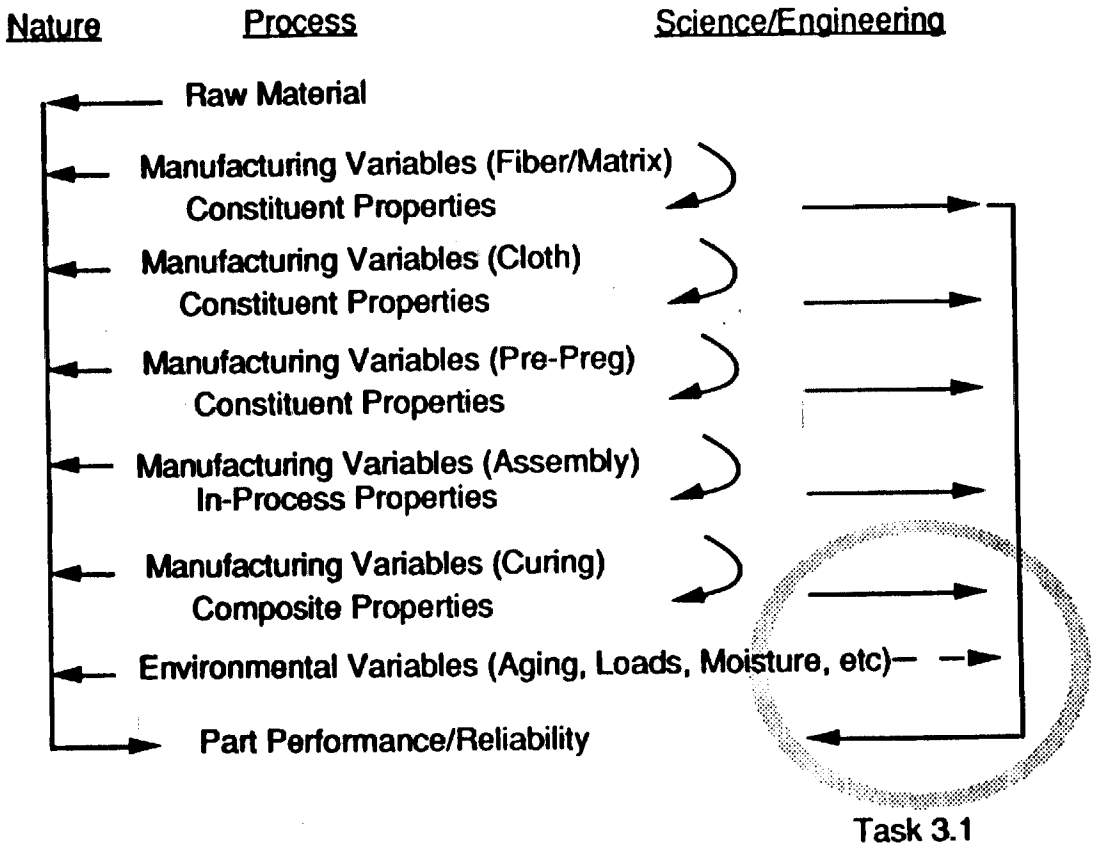






PDA ENGINEERING

HIERARCHY OF DATA



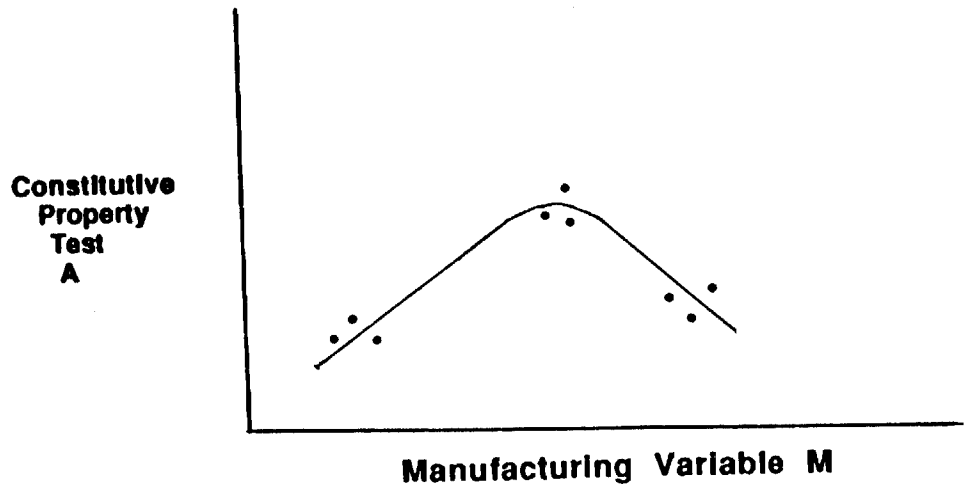
The joint SPIP 3.1/3.2 goal should be to apply the scientific method to relating measured properties to manufacturing variables and part performance.

pda ENGINEERING

PROBLEMS

- Large amounts of data continuously developed
- Six levels of relationships:
  - + If 4 individual tests and 3 manufacturing variables are involved at each of 6 process levels, to account for 3 values of each manufacturing variable, with 3 replications, the number of data points is:

    $9 \times (3 \times 4)^6 = 26{,}873{,}856$ experiments @\$500 → \$13.4B
  - + Experimental Planning needed to reduce scope of problem
  - + Computerized data base and query tools needed to handle data.



PDA ENGINEERING

RECOMMENDED PROJECT

- Relate manufacturing variables to constituent properties and composite properties.
- Relate constituent properties to composite ~~materials~~ properties.
- Search and find microstructural features to aid in developing relationships (physically based models)
- Develop statistically based predictive model to relate manufacturing variables to part performance and improve reliability estimates
- Establish a computerized material property relational data base to facilitate required studies and correlations
- Use "Taguchi" or other experimental planning methods to design test matrices. Implement within computerized relational data base.

APPENDIX H

ERIC STOKES

SELECTION OF ACCEPTANCE TESTS FOR CURED CARBON PHENOLICS

E.H. Stokes
Southern Research Institute
Birmingham, Alabama

Presented At

Solid Propulsion Integrity Program Industry Advisory Committee Meeting
Sacramento, California
November 14 – 15, 1991

Tlscr

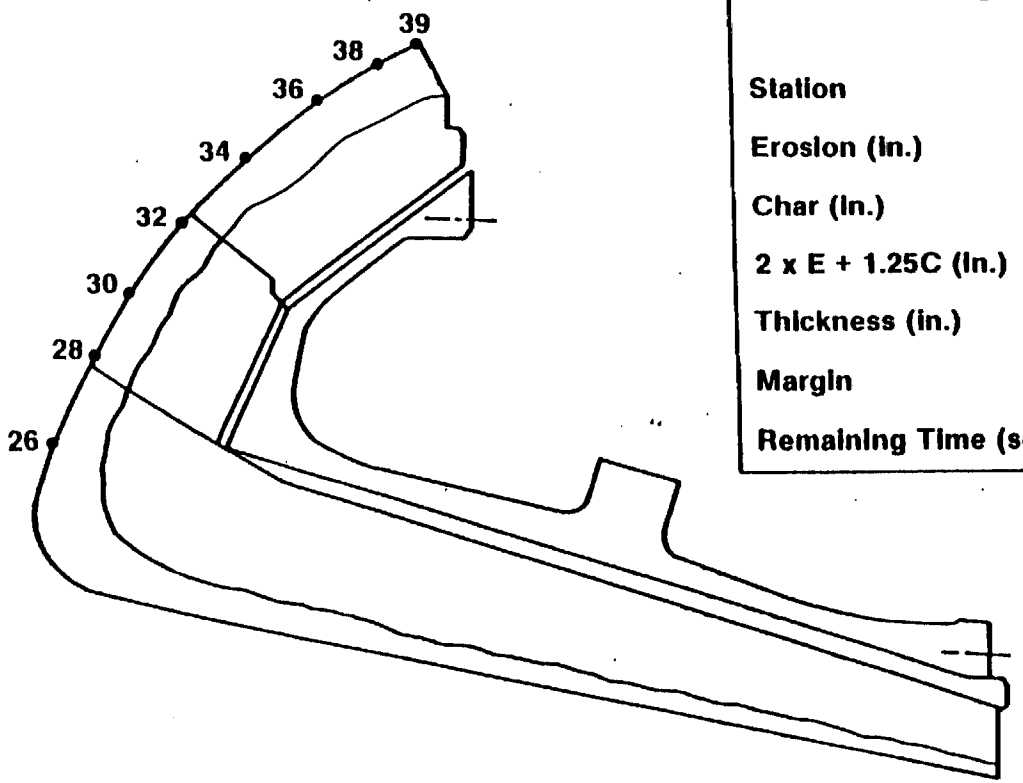
DESIRABLE PROPERTIES OF AN ACCEPTANCE TEST

1. Predictor of Failure Mode
2. Discriminator of "Good" vs. "Bad" Material
3. Accurate
4. Precise
5. Timely
6. Minimal Cost
7. Simple
8. Material Property

Material Properties Governing Key Material Events

EVENT	PRIMARY FACTORS	SECONDARY FACTORS
Erosion Rate	Yarn Carbonization Temperature Resin Content	Char Yield Filler Content
Char Depth (Back Face Temperature)	Thermal Conductivity	Heat of Ablation
Pocketing	Yarn Strength, ET Permeability f(AP Comp. Stress)	Char Yield (Moles of Gas Produced) Across Ply Thermal Expansion
Plylift	Low Temperature Permeability	Across Ply Tensile Strength
Delamination	Across Ply Contraction	Across Ply Tensile Strength/Modulus Char Yield
Thermostructural	In-Plane Strength/Modulus In-Plane Thermal Expansion	
Wedgeout	Across Ply Thermal Expansion Permeability	Char Yield (Moles of Gas Produced) Interlaminar Shear Strength

EROSION RATE



Minimum Margins of Safety

	Aft Ring
Station	34 (345 deg)
Erosion (in.)	1.39
Char (in.)	0.41
2 x E + 1.25C (in.)	3.29
Thickness (in.)	3.24
Margin	-0.02
Remaining Time (sec)	162

EROSION RATE

Possible Results

— Lower Margins of Safety

— Changes in Throat Dimensions (Thrust)

Properties That Result in Higher Susceptibilty to Event

o Higher Yarn Carbonization Temperatures Result in More Graphitic Structure in Yarn

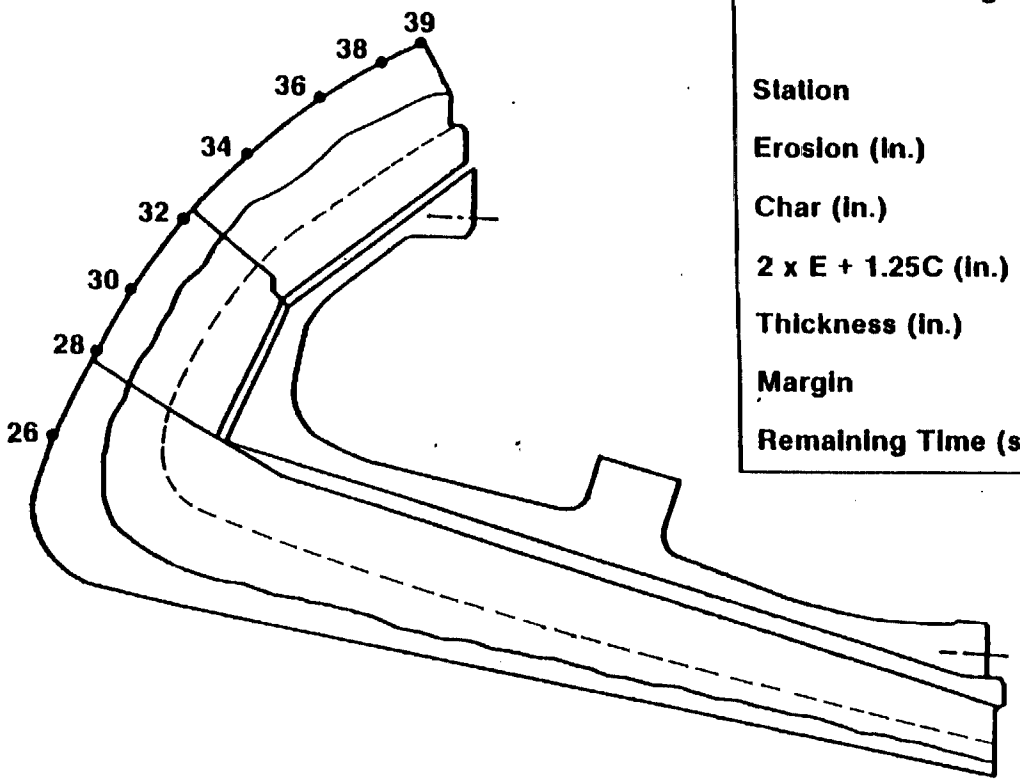
o Higher Resin Contents

Examples

o Many

view4

CHAR DEPTH



Minimum Margins of Safety

	Aft Ring
Station	34 (345 deg)
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Char (in.)	0.41
2 x E + 1.25C (in.)	3.29
Thickness (in.)	3.24
Margin	-0.02
Remaining Time (sec)	162

CHAR DEPTH
(BACKFACE TEMPERATURE)

Possible Results

— Lower Margins of Safety

— Destruction of Adhesive on Backface of Carbon

— Backface Gas Pressures

Properties That Result in Higher Susceptibilty to Event

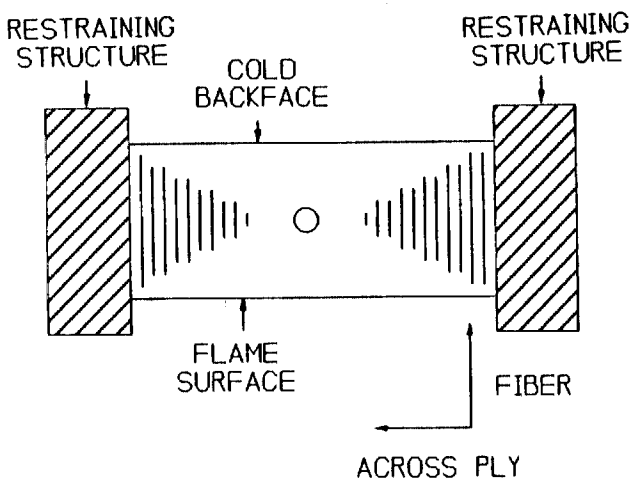
o Higher Thermal Conductivities

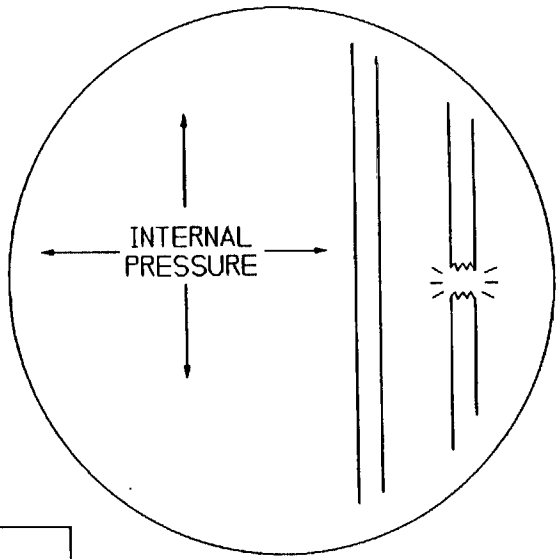
o Lower Heats of Pyrolysis

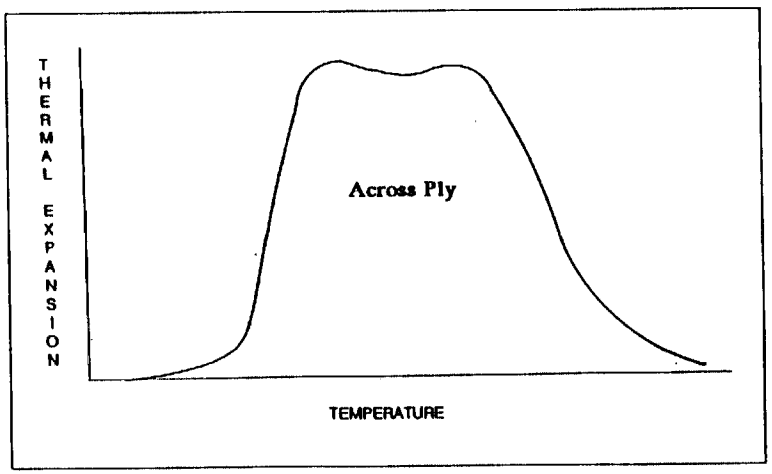
Examples

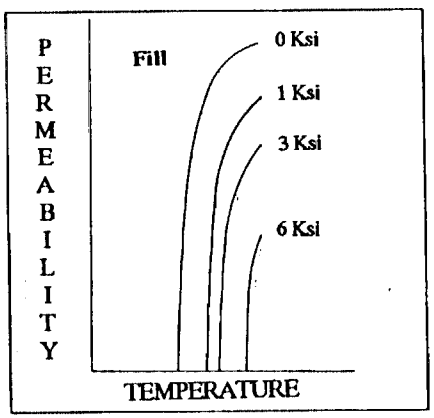
o Many

POCKETING


RESTRAINING STRUCTURE
COLD BACKFACE
RESTRAINING STRUCTURE
FLAME SURFACE
FIBER
ACROSS PLY


INTERNAL PRESSURE


THERMAL EXPANSION
Across Ply
TEMPERATURE


PERMEABILITY
Fill
0 Ksi
1 Ksi
3 Ksi
6 Ksi
TEMPERATURE

POCKETING

Possible Results

— Burn Through

— Higher Erosion Rates

— Disruption of Flow Field

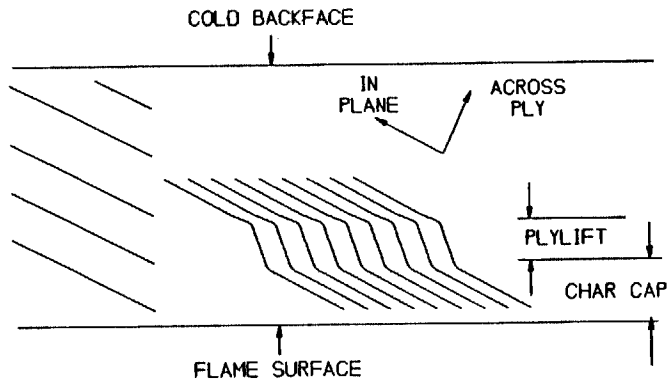
Properties That Result in Higher Susceptibilty to Event

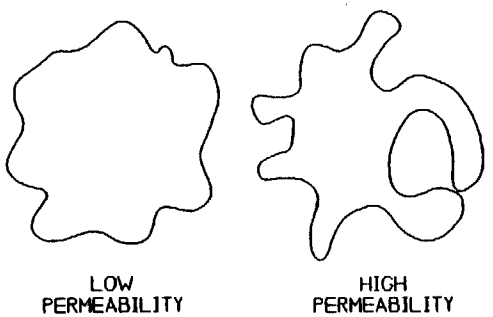
- o Lower Yarn Strengths
- o Lower Elevated Temperature In-Plane Permeability As a function of Across Ply Compressive Stress
- o Higher Across Ply Thermal Expansion
- o Lower Char Yield (Higher Moles of Gas Produced)

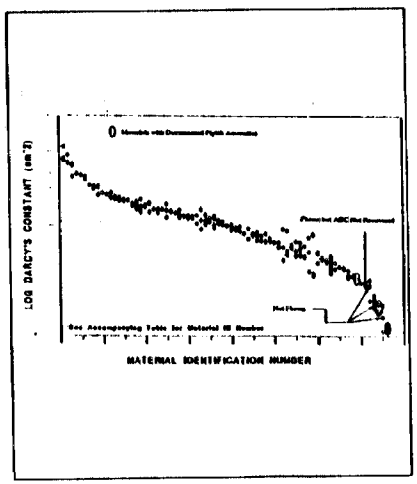
Examples

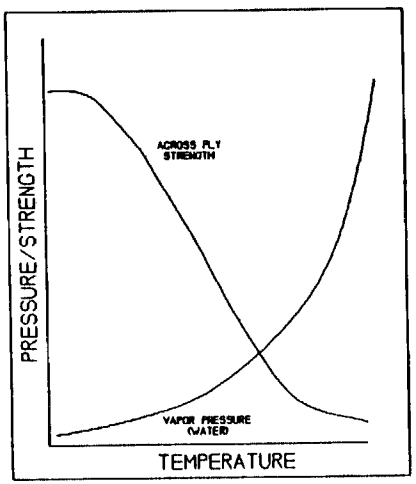
- 8A FWD Nose Ring
- 8A AFT Inlet Ring

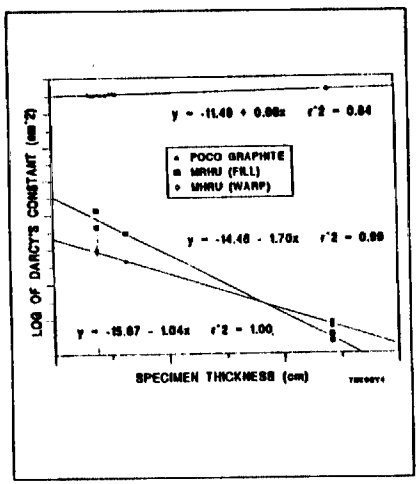
PLYLIFT


COLD BACKFACE
IN PLANE
ACROSS PLY
PLYLIFT
CHAR CAP
FLAME SURFACE

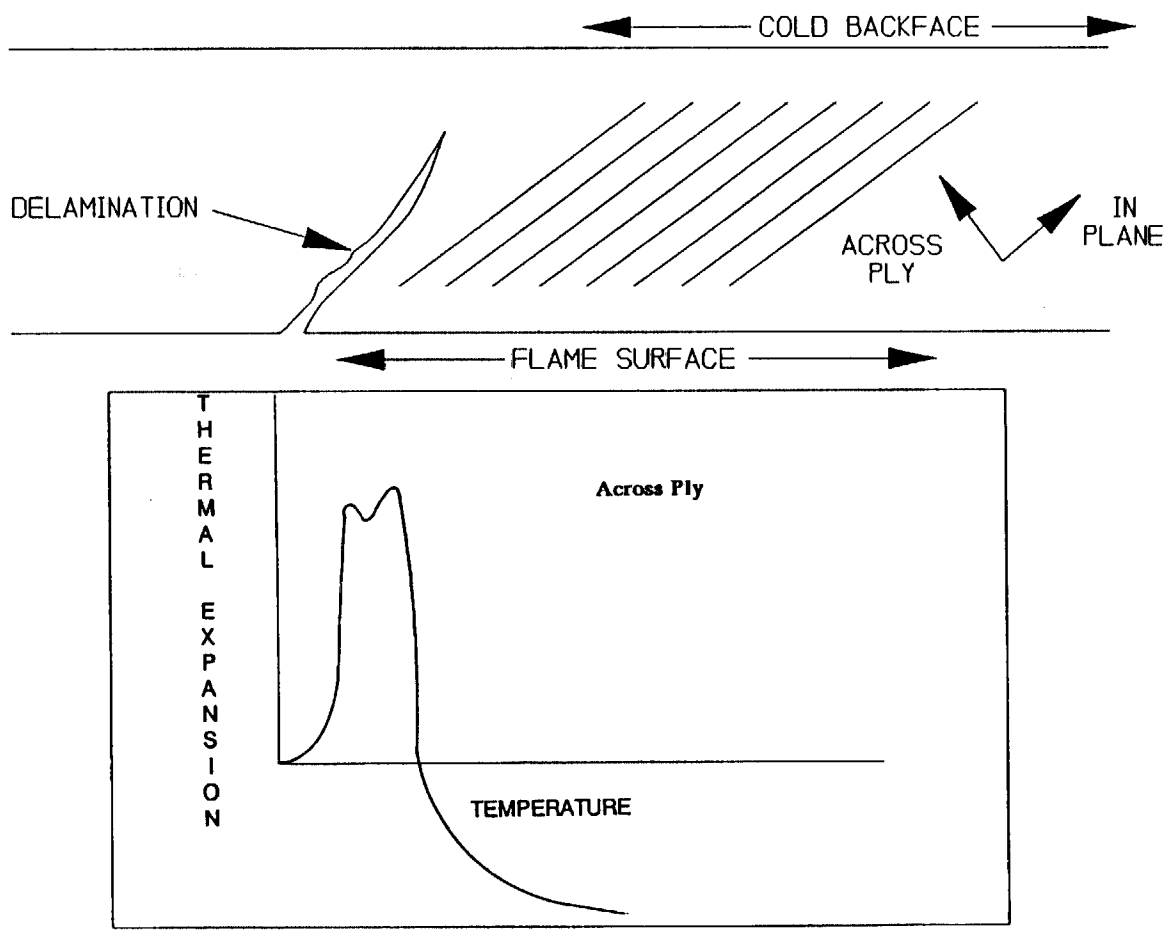

LOW PERMEABILITY
HIGH PERMEABILITY


LOG DARCY'S CONSTANT (m^2)
MATERIAL IDENTIFICATION NUMBER


PRESSURE/STRENGTH
ACROSS PLY STRENGTH
VAPOR PRESSURE (WATER)
TEMPERATURE


y = -11.48 + 0.66x r^2 = 0.84
POCO GRAPHITE
MRHU (FILL)
MHRU (WARP)
y = -14.46 - 1.70x r^2 = 0.99
y = -15.67 - 1.84x r^2 = 1.00
LOG OF DARCY'S CONSTANT (m^2)
SPECIMEN THICKNESS (cm)

DELAMINATIONS



PLYLIFT
(CHAR CAP REMOVAL)

Possible Results

— Burn Through

— Higher Erosion Rates

— Disruption of Flow Field

Properties That Result in Higher Susceptibilty to Event

o Lower Room Temperature Permeability

o Lower Across Ply Tensile Strength (Minor Role)

o Higher Volatiles Content (Only Under Some Conditions)

Examples

- ETM-1A AEC
- FSM-1 AEC
- TEM-6 AEC
- 15B COWL

view8

DELAMINATIONS

Possible Results

— Lower Margins of Safety

— Greater Char Depth

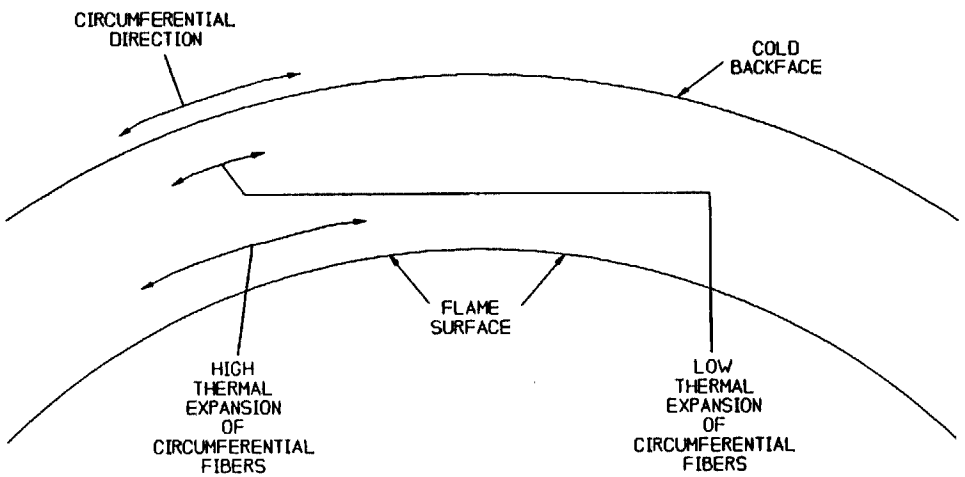
Properties That Result in Higher Susceptibilty to Event

- o Higher Across Ply Contraction
- o Lower Across Ply Tensile Strength
- o Lower Char Yield

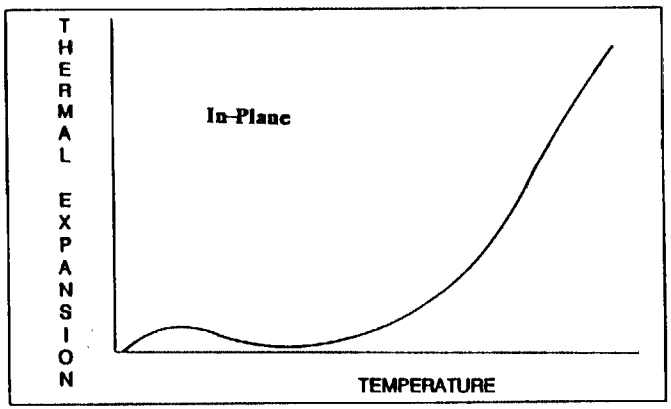
Examples

- Many

THERMOSTRUCTURAL FAILURE



RESULT: Circumferential Fibers at Low Temperature In Tension. If Tensile Forces Exceed Strength of Fibers, Fibers Fail.



THERMOSTRUCTURAL

Possible Results

— Yarn Breakage

— Reduced Structural Integrity

Properties That Result in Higher Susceptibilty to Event

o High Yarn Thermal Expansion

o Low Yarn Strength

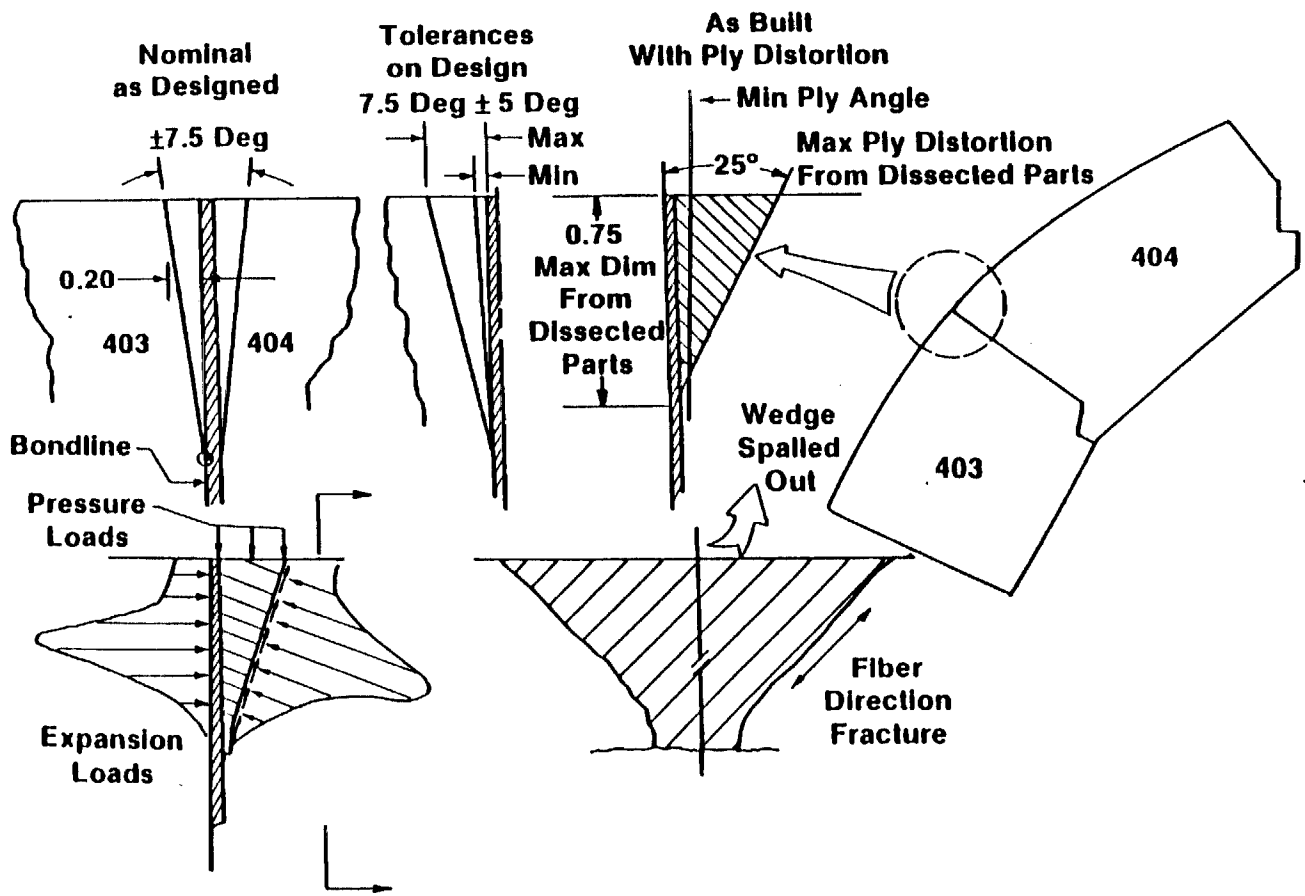
o High Yarn Modulus

Examples

o None With Carbon Phenolic

o Some With Carbon-Carbons

WEDGEOUT


Nominal
as Designed
±7.5 Deg
Tolerances
on Design
7.5 Deg ± 5 Deg
Max
Min
As Built
With Ply Distortion
Min Ply Angle
25°
Max Ply Distortion
From Dissected Parts
0.75
Max Dim
From
Dissected
Parts
0.20
403
404
Bondline
Pressure
Loads
Expansion
Loads
Wedge
Spalled
Out
404
403
Fiber
Direction
Fracture

WEDGEOUT

Possible Results

— Lower Margins of Safety

— Greater Char Depth

Properties That Result in Higher Susceptibilty to Event

- o Higher Across Ply Thermal Expansion
- o Lower Permeability
- o Lower Interlaminar Shear Strength

Examples

- 10B FWD Nose Ring
- 10B AFT Inlet Ring

EXAMPLES OF SOME TESTS THAT CAN GIVE SOME INSIGHT INTO PRIMARY PROPERTIES

KEY PROPERTY	TMA	TGA	ELECTRICAL RESISTIVITY	FILL TENSILE	RT PERM	PLY THICKNESS	BULK DENSITY	EXTENDED VOLATILES
Yarn Carbonization Temperature			?	?				
Resin Content		O	?			O	O	
Thermal Conductivity			O					
Yarn Strength			?	●				
Yarn Modulus			?	●				
Yarn Thermal Expansion	●							
Low Temperature Permeability	?				●			O
Across Ply Thermal Contraction	O	?			?			
Elevated Temperature Permeability	O	?						
Across Ply Thermal Expansion	O							

● Direct Measurement

O Indirect Measurement

? Possible Correlation

APPENDIX I

TOM PARAL

POLYCARBON, Inc.®

A MEMBER OF THE SIGRI GROUP

North American Rayon
Carbonizable Finish Trials
5-Ply Carbon Yarn Properties

	Carbonizable Finish Level .65%	1.0%	Control
Yarn weight (g/m)	0.33	0.34	0.31
Break strength (kg)	2.39	1.81	10.42
Twist (tpm)	90.6	86.6	90.6
Moisture (%)	0.20	0.17	0.22
Specific gravity (g/cc)	1.47	1.46	1.47
Ash (%)	0.13	0.14	0.12
Sodium (ppm)	235	145	190
Carbon (%)	99.7	99.9	99.5

11-13-91

T. A. Paral

APPENDIX J

KEN DRAKE

AGENDA

o	AIR FORCE PHILLIPS LABORATORY CAPABILITIES	LES TEPE
o	AEROSPACE MATERIALS EVALUATION CAPABILITIES	DAVID SUTTON
o	ISSUES AND CONCERNS	KEN DRAKE LES TEPE
o	DATA BASE DEMONSTRATION	KEN DRAKE

ISSUES AND CONCERNS

- PRODUCT IDENTIFICATION
- ENVIRONMENTAL CONCERNS
- PRODUCT SHELFLIFE AND SHELFLIFE EXTENSION
- RAW MATERIALS ACCEPTANCE TESTING
- TAG END TESTING

DATA BASE DEMONSTRATION

- THIS DATA BASE WAS CREATED BY THE OAK RIDGE NATIONAL LABORATORY FOR WRDC ON THE THERMOPLASTICS MATERIALS PROGRAM

- THE DEMONSTRATION IS AN EXAMPLE OF THE NEW DATA BASE CALLED "ABLATIVE MATERIALS DATA BASE" BEING CREATED BY THE AEROSPACE CORPORATION IN CONJUNCTION WITH THE SPIP PROGRAM

- THE ABLATIVE MATERIALS DATA BASE WILL INCLUDE MATERIALS DATA FROM RAYON THRU END ITEM DESIGN ALLOWABLES. COMPLETION IS EXPECTED TO TAKE ONE TO TWO YEARS

- THE PROGRAM NAMED "M VISION" WILL BE THE CORE PROGRAM WITH PC INPUT AND OUT PUT ON DISKS

APPENDIX K

DAVE SUTTON

AEROSPACE TECHNOLOGY CENTER CAPABILITIES

I. PREPREG TESTING
   - A. COMPOSITION
   - B. PHYSICAL PROPERTIES

II. CURED SPECIMEN TESTING
   - A. COMPOSITION
   - B. PHYSICAL PROPERTIES
   - C. THERMAL PROPERTIES
   - D. NONDESTRUCTIVE EVALUATION

III. SAMPLING

IV. ABLATION TESTING

V. SUMMARY

RESIN MATRIX COMPOSITE CHARACTERIZATION

PREPREG TESTING

COMPOSITION

- FOURIER TRANSFORM INFRARED SPECTROMETRY (FTIR)
  - DETERMINES INFRARED ABSORPTION OF EXTRACTS
  - BASIC FUNCTIONAL CHEMICAL GROUPS IDENTIFIED
  - VERIFICATION OF BASIC CHEMICAL COMPOSITION
- DIFFERENTIAL SCANNING CALORIMETRY (DSC)
  - PHASE CHANGES, CHEMICAL CHANGES
- THERMAL GRAVIMETRIC ANALYSIS (TGA)
- RESIN CONTENT (SOLVENT EXTRACTION)
- FLOW

RESIN MATRIX COMPOSITE CHARACTERIZATION

CURED SPECIMENS

COMPOSITIONAL ANALYSIS

- **THERMAL GRAVIMETRIC ANALYSIS**
  - RESIDUAL VOLATILES
  - SOLVENT, WATER, PHENOL, FORMALDEHYDE
- **MOISTURE ANALYZER**
  - PERCENT MOISTURE
- **DEGREE OF CURE**
- **RESIN CONTENT (ACID DIGESTION)**

RESIN MATRIX COMPOSITE CHARACTERIZATION

CURED SPECIMENS

PHYSICAL PROPERTIES

- TENSILE STRENGTH
- TENSILE MODULUS
- ELONGATION
- INTERLAMINAR SHEAR STRENGTH
- BARCOL HARDNESS
- POROSITY
- MICROSTRUCTURE

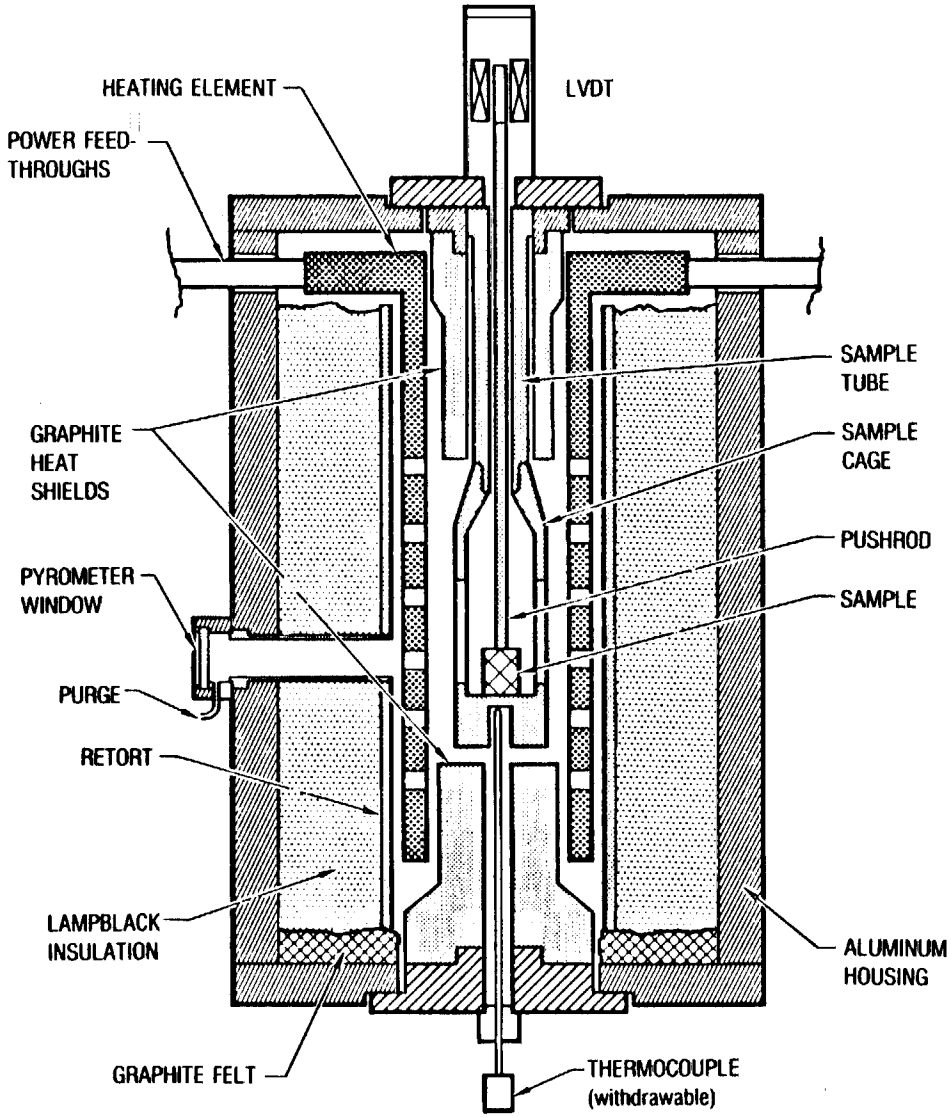
RESIN MATRIX COMPOSITE CHARACTERIZATION

CURED SPECIMENS

THERMAL PROPERTIES

- **COEFFICIENT OF THERMAL EXPANSION**
  - THERMAL MECHANICAL ANALYZER (TMA)
  - DILATOMETER
- **GLASS TRANSITION TEMPERATURE**
  - DIFFERENTIAL SCANNING CALORIMETER

HIGH TEMPERATURE DILATOMETER



RESIN MATRIX COMPOSITE CHARACTERIZATION

NONDESTRUCTIVE EVALUATION

- **ULTRASONICS**
  - DEBONDS, VOIDS ,CRACKS
  - THICKNESS
- **THERMOGRAPHY**
  - DIFFUSIVITY
  - DELAMINATIONS
- **RADIOGRAPHY OF SAMPLES**
  - (1 FOOT MAXIMUM DIMENSION)
  - DIMENSIONAL ANALYSIS
  - VOIDS, FOREIGN MATERIAL

RESIN MATRIX COMPOSITE CHARACTERIZATION

SAMPLING

- ALL SPECIFIED TESTS ARE SENSITIVE TO LOCATION
  - UNEVEN CURING DUE TO LONG LAY UP TIMES
  - MULTIPLE DEBULKINGS
- CURED SAMPLES MUST BE REPRESENTATIVE OF THE PART
  - TAG ENDS NOT ALWAYS THE BEST
  - DESIGN PART TO INCLUDE SAMPLE POINTS
- TGA, DCA, FTIR USE SMALL SAMPLES
  - MULTIPLE TESTS REQUIRED

ABLATION TESTING

- **UNIQUE APPARATUS**
  - 30 KW ARCJET
  - CONTROLLED ENTHALPY
  - CONTROLLED ATMOSPHERE
  - STRESSED SAMPLES

- **DIAGNOSTICS**
  - VIDEO RECORDING
  - THERMAL IMAGING
  - FAST TEMPERATURE MONITORS

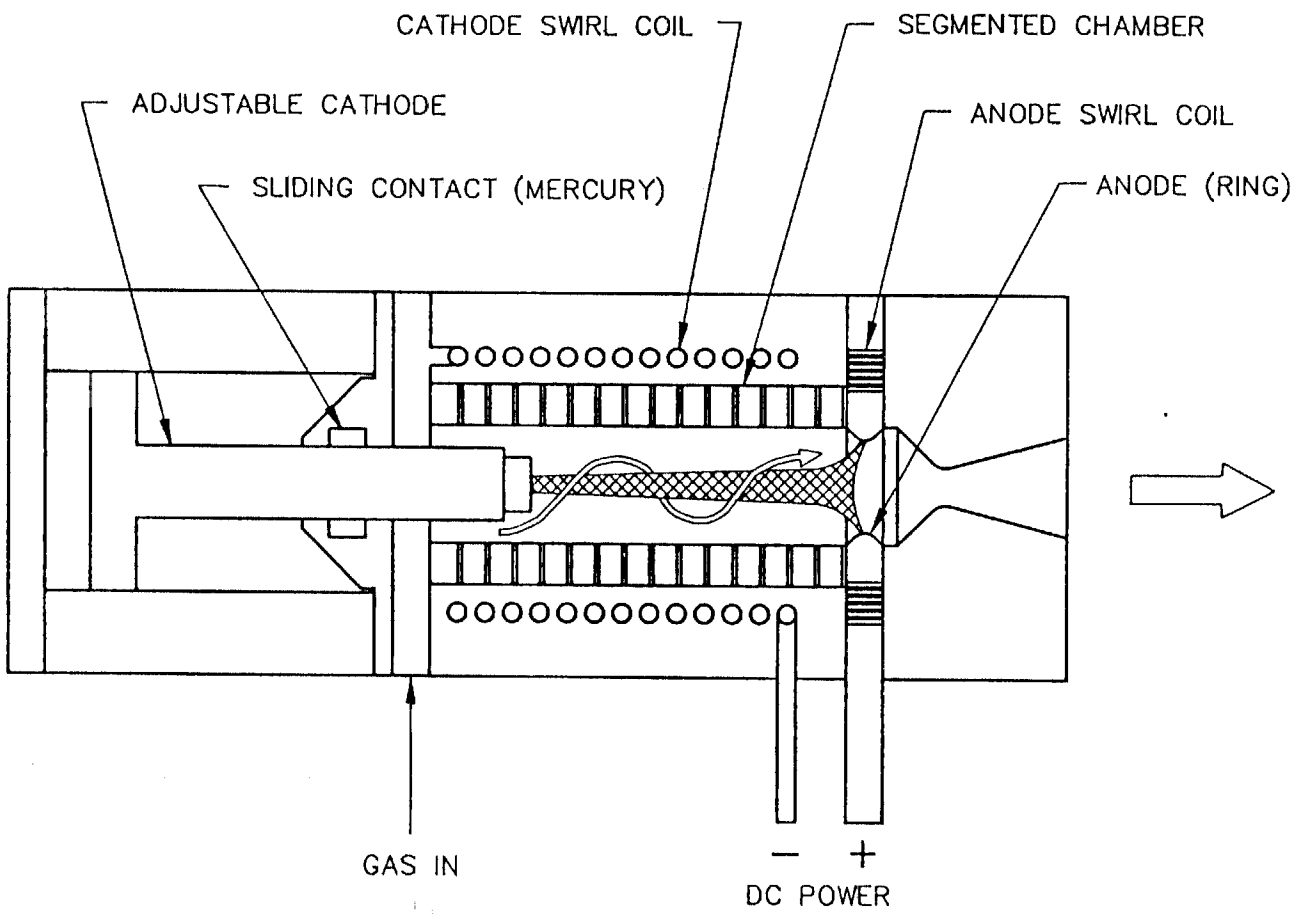
RESIN MATRIX COMPOSITE CHARACTERIZATION

ABLATION TESTING

- **UNIQUE APPARATUS**
  - 400 KW ARCJET
  - 10,000 BTU/FT**2-SEC ON TARGET
  - O.5 X 2.0 IN TARGETS
  - STRESSED SAMPLES

- **DIAGNOSTICS**
  - FAST FRAMING VIDEO RECORDING
  - THERMAL IMAGING
  - FAST TEMPERATURE MONITORS

400 KW ARC HEATER



RESIN MATRIX COMPOSITE CHARACTERIZATION

SUMMARY

- DESIGN PARTS WITH REPRESENTATIVE SAMPLE POINTS

- CORRELATE FUNCTIONAL TESTING WITH CHARACTERIZATION

  DEFINE A REPRESENTATIVE FUNCTIONAL TEST (ABLATION?)

  IDENTIFY CHARACTERIZATIONS THAT DETERMINE PERFORMANCE (VOLATILE CONTENT, VOIDS, POROSITY, SHEER STRENGTH)

  CORRELATE MEASURED PROPERTIES WITH FUNCTION

- SEEK A MINIMUM SET OF CHARACTERIZATION TESTS

  SIMPLE, AVAILABLE, FAST, INEXPENSIVE

  SUFFICIENT TO PROJECT FUNCTIONAL BEHAVIOR

APPENDIX L

KEN DeVANE

BP Chemicals (Hitco), Inc.
Fibers & Materials
Gardena

Carbon Assay Testing
SPIP
Aerojet, Sacramento

14 November 1991

KEN DE VANE
GEORGE PEASLEY

Carbon Assay Testing
Agenda

- Background
- Preliminary work at BP
- Standard/Machine/Technician comparison
- Moisture
- System capability
- Conclusions

Carbon Assay Testing
Background

- Concerns about test precision and accuracy
  - Variation between labs
  - Variation between methods/equipment
  - Possible variation over time
- Standard selection
  - Fabric
  - Particulate

SPIP - CARBON ASSAY TESTING CALIBRATION ROUND ROBIN TEST RESULTS (502-099/191-A-L)(1)

LABORATORY

RUN	A	B	C
1	95.2	97.05	95.98
2	95.2	97.22	96.12
3	95.2	97.08	96.42
4	95.3		96.18
5	95.6		96.89
X	95.3	97.12	96.32
S	0.17	0.09	0.36

(1) NBS Carbon Assay 96.81 = 0.38

R&DD

CARBON ASSAY TESTING

LOCKHEED

Round Robin Testing

Identification		Leco (1) (CR-12)	Leco (1) (CHN-600)	Polycarbon (2) (CR-12) Run 1	Polycarbon (2) (CR-12) Run 2	BP/Hitco (1) (CHN-600)
ASRM Task 1						
Polycarbon, C-5 Yarn						
NSC "M"	High Temp.	99.89 (0.21)	99.68 (0.14)	99.1	98.8	99.3 (0.35)
NSC "M"	Std. Temp.	98.82 (0.59)	99.11 (0.19)	98.0	98.6	99.2 (0.15)
NSC "M"	Low Temp.	97.20 (0.16)	96.70 (0.15)	97.7	97.5	98.6 (0.10
BP/Hitco						
H-4175-2A	High Temp.	100.0 (0.80)	100.04 (0.12)	98.5	98.8	99.6 (0.31)
S-4175-4A	Std Temp.	98.30 (0.41)	98.34 (0.35)	97.1	97.5	98.7 (0.10)
L-4178-5B	Low Temp.	96.36 (0.53)	97.03 (0.14)	97.0	96.1	97.9 (0.20)

(1) Calibration with WCA Fiber

(2) Calibration with NBS Coke, WCA measured 99.1 & 99.2

R&DD

CARBON ASSAY TESTING

LOCKHEED

Round Robin Testing for Carbon Assay
Leco Technical Services Laboratory

	Fabric Identification		Vendor Certification (1)	Leco CR-12 (2) x	Leco CR-12 (2) (s)	Leco CHN-600 (2) x	Leco CHN-600 (2) (s)
1.	CSA/0534		99.7/98.9	93.84	(0.47)	93.89	(0.27)
2.	CSA/0539		99.5/98.3	93.35	(0.16)	94.28	(0.56)
3.	CSA/0567		97.8/97.9	93.32	(0.36)	94.25	(0.10)
		$\bar{x}$	98.7	93.50		94.14	
4.	CCA3/42063		97.5/97.6	94.27	(0.47)	94.33	(0.35)
5.	CCA3/42099		97.6/97.2	93.18	(0.28)	93.89	(0.19)
6.	CCA3/42352		97.3/96.0	92.67	(0.24)	93.13	(0.15)
		$\bar{x}$	97.2	93.37		93.78	
7.	VCX-13		99.8/99.9	99.00	(0.17)	99.30	(0.15)
8.	10B		96.2/97.5	89.44	(0.48)	89.34	(0.27)
9.	WCA		99.9	99.77	(0.42)	99.94	(0.14)

(1) Outside/Inside of Roll

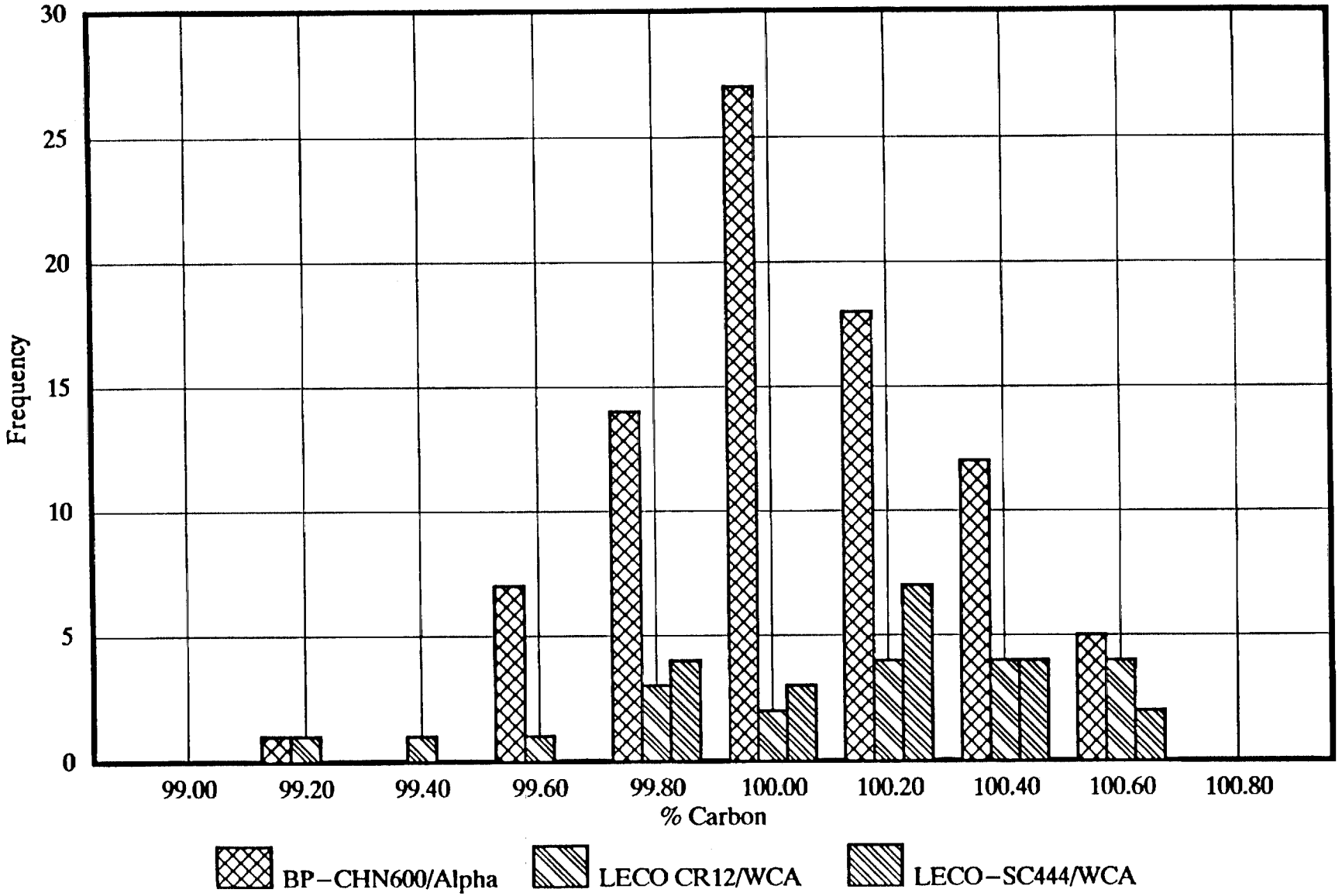
(2) n = 3, Calibration with WCA Fabric

Carbon Assay Testing
BPCHI Preliminary Work

- CHN 600 / Alpha Resources Graphite
  - 84 individual carbon assay values as both standard and unknown.
- Compared results to LECO / WCA with CR12 & SC444.
- CHN600/Alpha & CR12/LECO had same range.
- Conclusion : need to compare Alpha & WCA on the same machine, same method.

Carbon Assay Testing Comparison

Compare BPCHI/Alpha to LECO/WCA



(e.g. Observation at 99.2 means 1 between 99.2 & 99.2)

Carbon Assay Testing
BPCHI F&M Effort

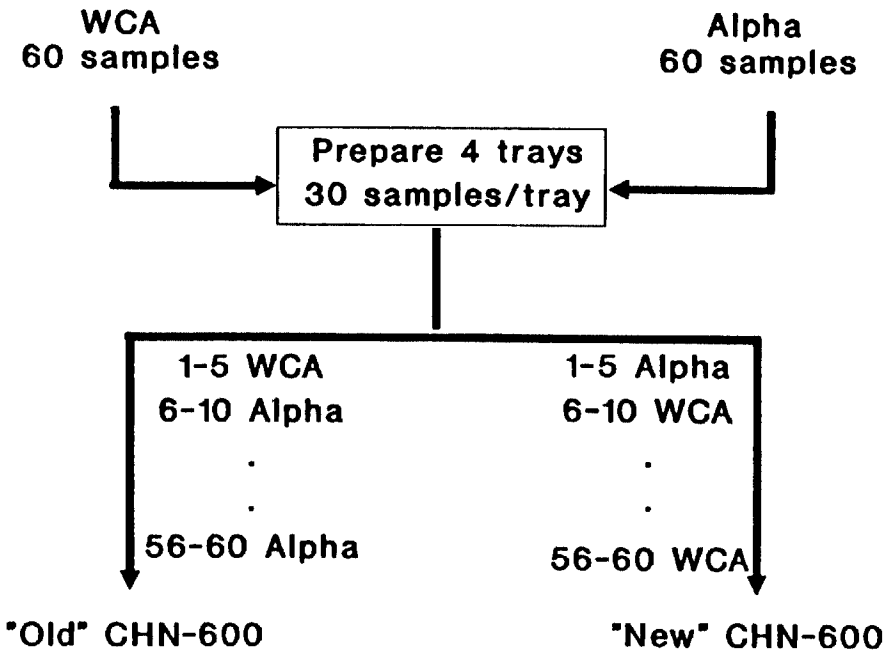
- Identify possible sources of variation.

- Investigate most likely sources
  - Standard
  - Machine
  - Moisture
  - Possible others in future.

- Standard selection issue:
  - Is it more accurate?
  - Is it more precise?

Carbon Assay Testing
Standard Comparison

- Compare
  - 3 Technicians
  - 2 Machines (both CHN 600)
  - 2 Standards (Alpha & WCA)
  - No calibration within sets (set size 60, 30, 30, 30, 30)



BPCHI F&M, Gardena

Results

ANALYST	SAMPLE	OLD CHN ALPHA	OLD CHN W C A	OLD CHN Dif(A-W)	NEW CHN ALPHA	NEW CHN WCA	NEW CHN Dif(A-W)
Tech 1 1-30	Avg	99.81	99.77	0.04	100.15	100.31	-0.17
	Stds	0.32	0.25	0.08	0.48	0.49	-0.01
	Min	99.30	99.20	0.10	99.25	99.66	-0.41
	Max	100.29	100.15	0.14	100.89	101.15	-0.26
	Range	0.99	0.95	0.04	1.64	1.49	0.15
Tech 1 31-60	Avg	99.41	99.83	-0.42	100.24	100.46	-0.23
	Stds	0.36	0.27	0.09	0.44	0.37	0.07
	Min	98.92	99.25	-0.33	99.52	99.87	-0.35
	Max	100.16	100.22	-0.06	100.85	101.04	-0.19
	Range	1.24	0.97	0.27	1.33	1.17	0.16
Tech 1 1-60 Combine	Avg	99.61	99.80	-0.19	100.19	100.39	-0.20
	Stds	0.39	0.26	0.14	0.45	0.43	0.02
	Min	98.92	99.20	-0.28	99.25	99.66	-0.41
	Max	100.29	100.22	0.07	100.89	101.15	-0.26
	Range	1.37	1.02	0.35	1.64	1.49	0.15

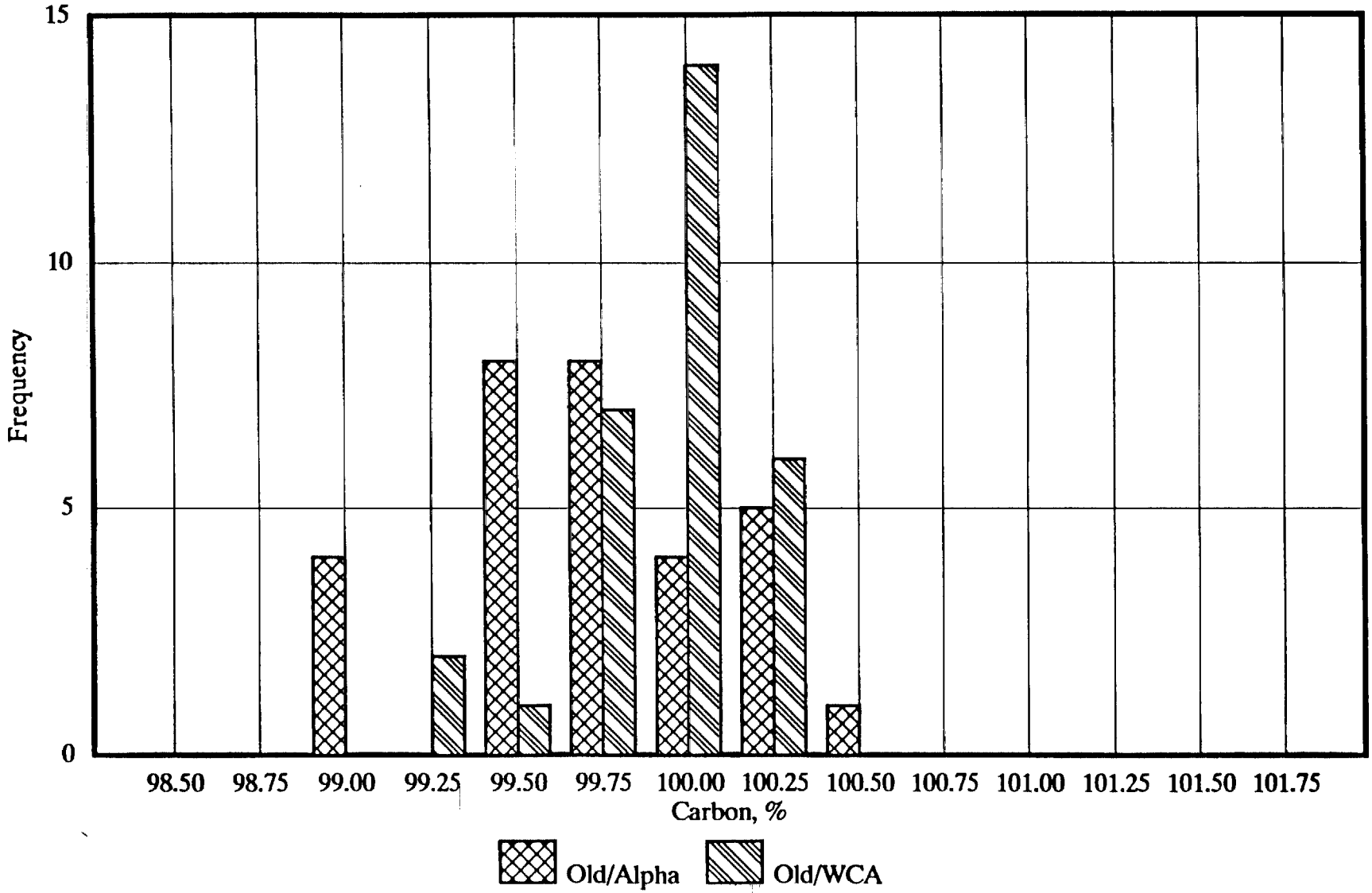
ANALYST	SAMPLE	OLD CHN ALPHA	OLD CHN W C A	OLD CHN Dif(A-W)	NEW CHN ALPHA	NEW CHN WCA	NEW CHN Dif(A-W)
Tech 2 1-30	Avg	101.12	100.68	0.44	99.89	99.71	0.18
	Stds	0.23	0.17	0.05	0.50	0.47	0.03
	Min	100.60	100.42	0.18	99.22	98.71	0.51
	Max	101.45	101.02	0.43	100.82	100.48	0.34
	Range	0.85	0.60	0.25	1.60	1.77	-0.17
Tech 2 31-60	Avg	99.33	99.56	-0.23	100.01	100.19	-0.18
	Stds	0.24	0.24	-0.00	0.44	0.42	0.02
	Min	98.94	99.20	-0.26	99.42	99.45	-0.03
	Max	99.80	100.09	-0.29	100.82	101.24	-0.42
	Range	0.86	0.89	-0.03	1.40	1.79	-0.39

ANALYST	SAMPLE	OLD CHN ALPHA	OLD CHN W C A	OLD CHN Dif(A-W)	NEW CHN ALPHA	NEW CHN WCA	NEW CHN Dif(A-W)
Tech 3 1-30	Avg	99.81	99.78	0.03	100.75	100.31	0.45
	Stds	0.28	0.30	-0.02	0.53	0.80	-0.27
	Min	99.30	99.20	0.10	100.02	98.45	1.57
	Max	100.24	100.24	0.00	101.89	101.38	0.51
	Range	0.94	1.04	-0.10	1.87	2.93	-1.06
Tech 3 31-60	Avg	99.73	98.80	0.93	100.52	99.91	0.61
	Stds	0.29	0.24	0.05	0.47	0.61	-0.15
	Min	99.21	98.35	0.86	99.92	99.03	0.89
	Max	100.11	99.13	0.98	101.56	100.90	0.66
	Range	0.90	0.78	0.12	1.64	1.87	-0.23

BPCHI F&M, Gardena

Carbon Assay Standard Comparison

WCA and Alpha Graphite w/CHN600

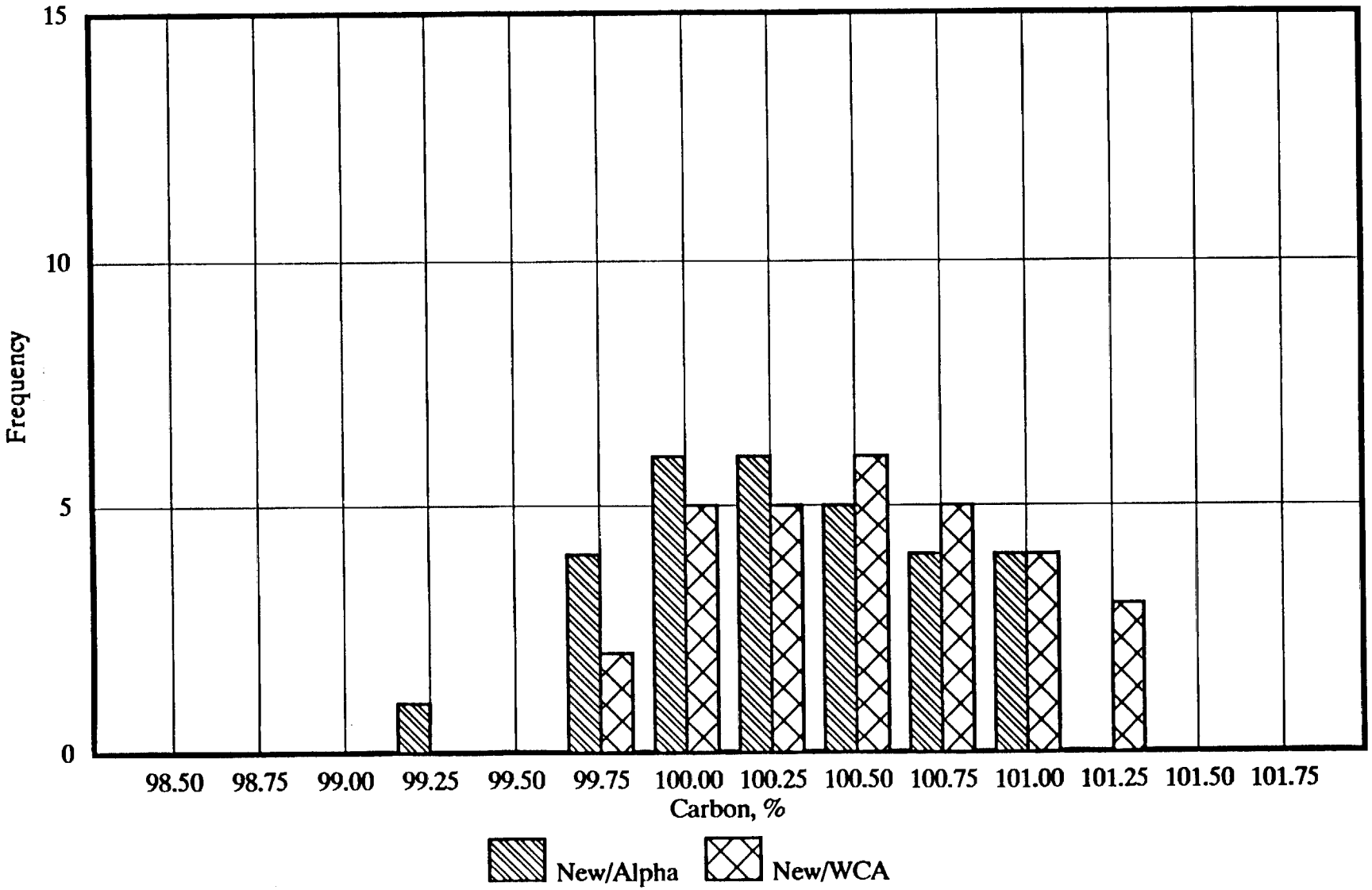


One observation at 100.0 means one point between 99.75 and 100.0

BPCHI F&M, Gardena

Carbon Assay Standard Comparison

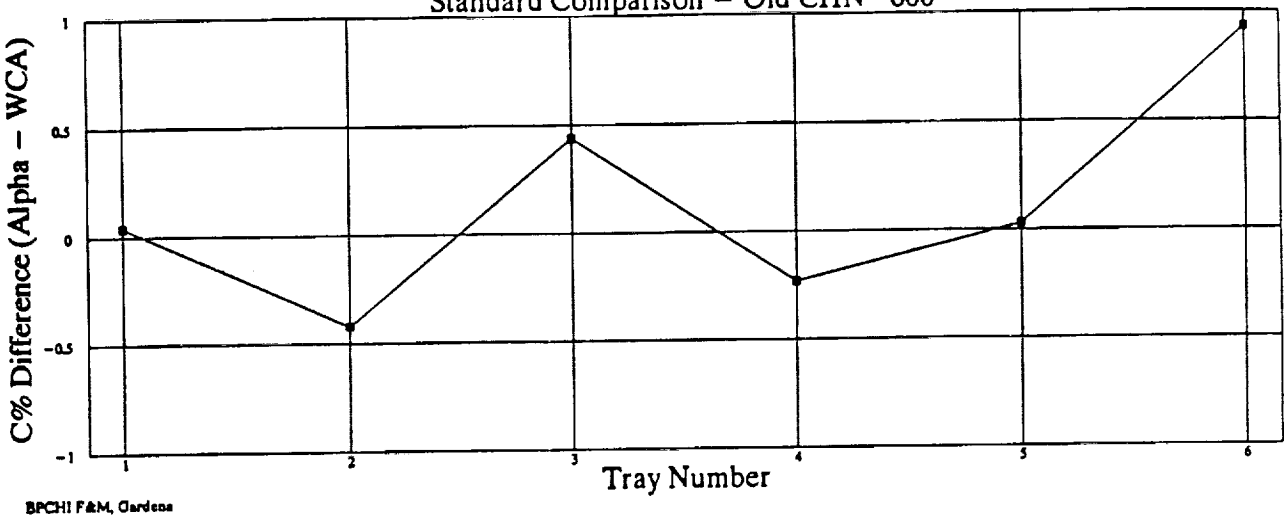
WCA and Alpha Graphite w/CHN600



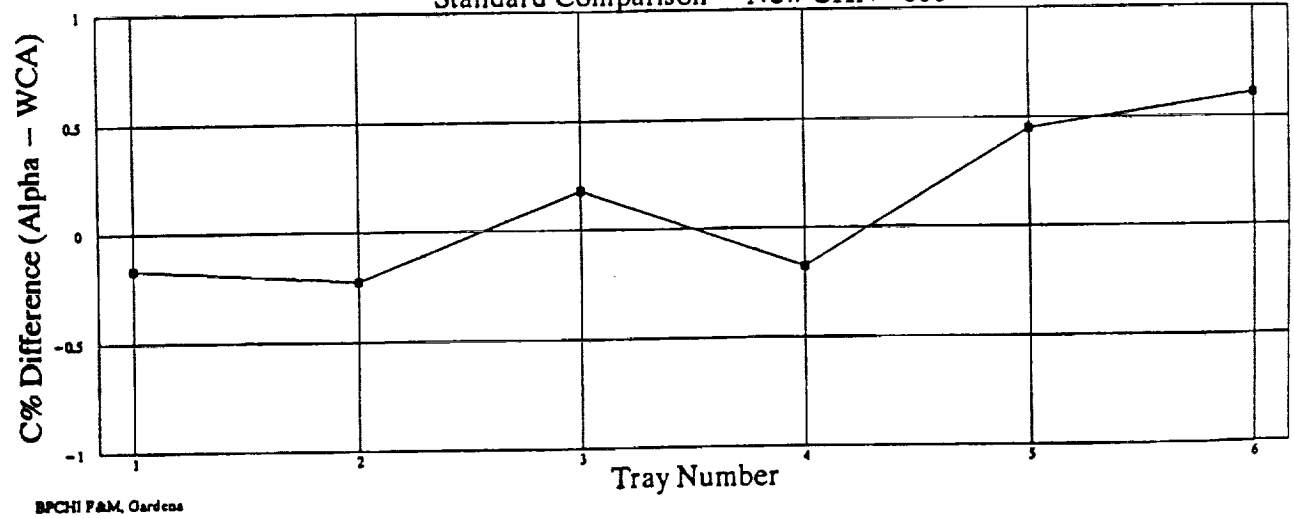
N=30 per combination
BPCHI F&M, Gardena

Comparison of Standards
Average Carbon %

Carbon Assay Testing
Standard Comparison – Old CHN–600



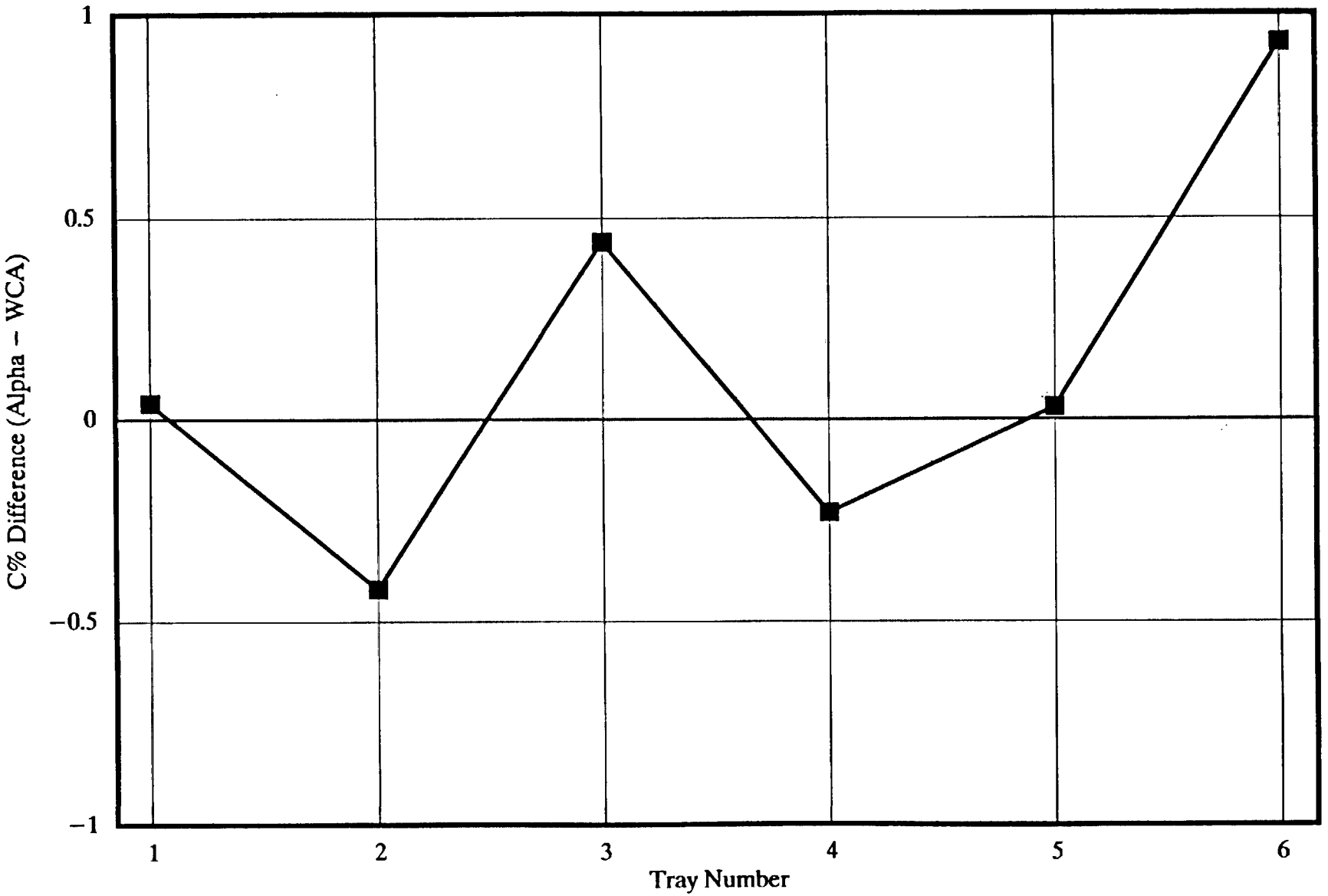
Carbon Assay Testing
Standard Comparison – New CHN–600



BPCHI F&M, Gardena

Carbon Assay Testing

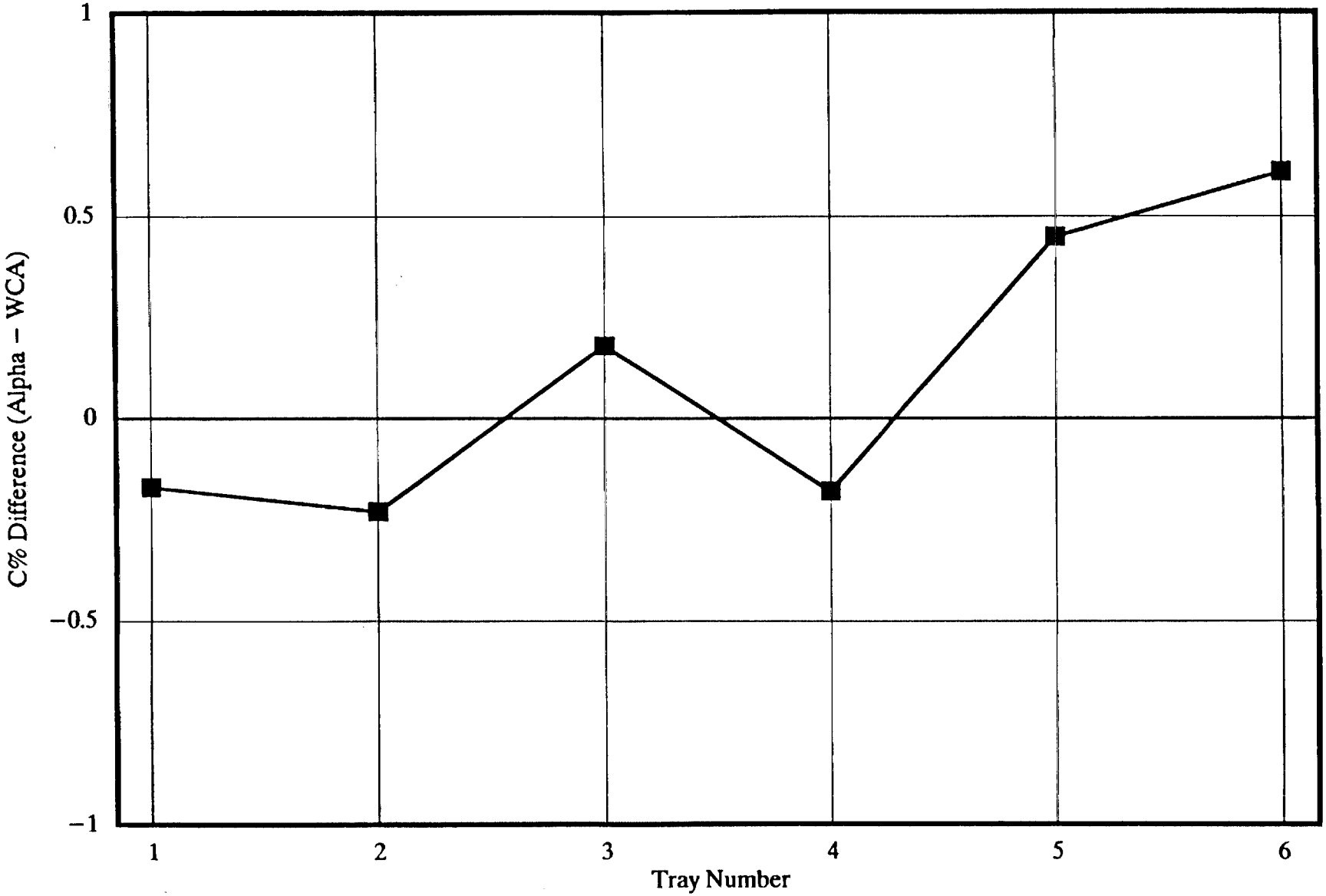
Standard Comparison – Old CHN–600



BPCHI F&M, Gardena

Carbon Assay Testing

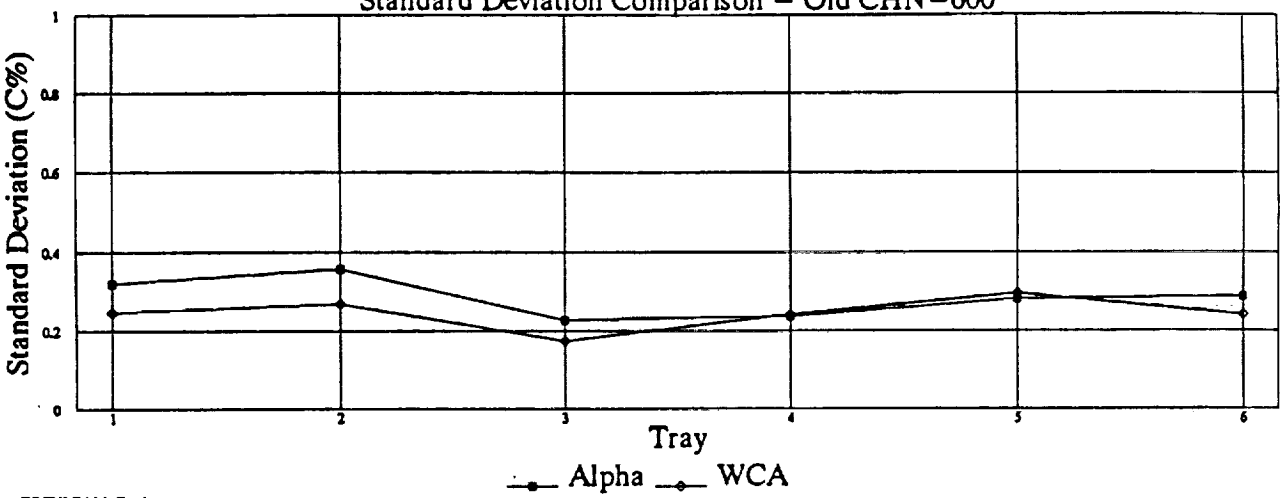
Standard Comparison – New CHN–600



BPCHI F&M, Gardena

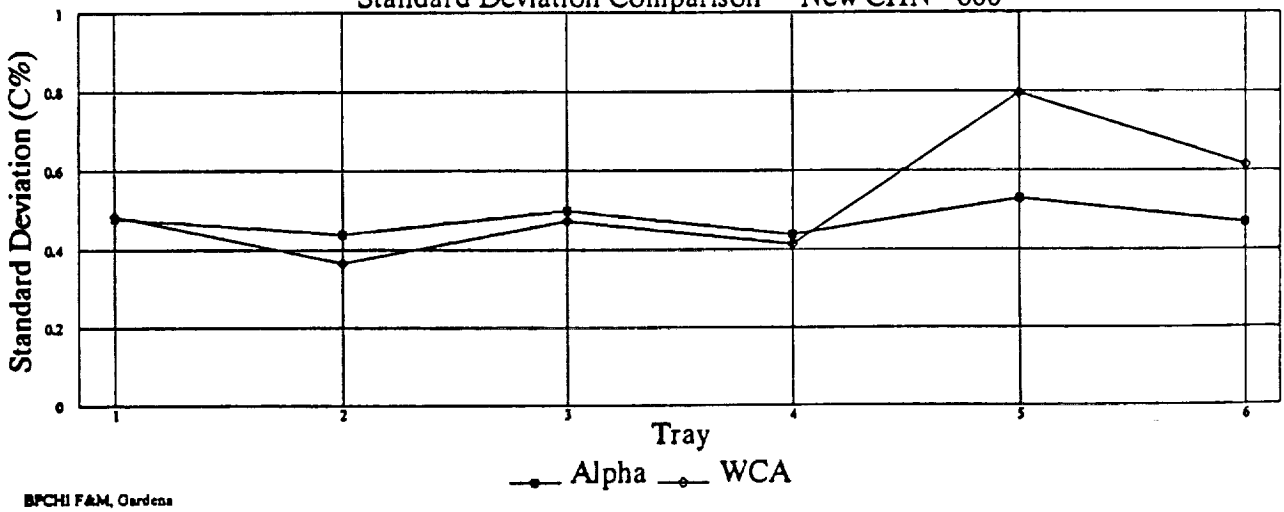
Comparison of Standards
Standard Deviation

Carbon Assay Testing
Standard Deviation Comparison – Old CHN-600



BPCHI F&M, Gardena

Carbon Assay Testing
Standard Deviation Comparison – New CHN-600

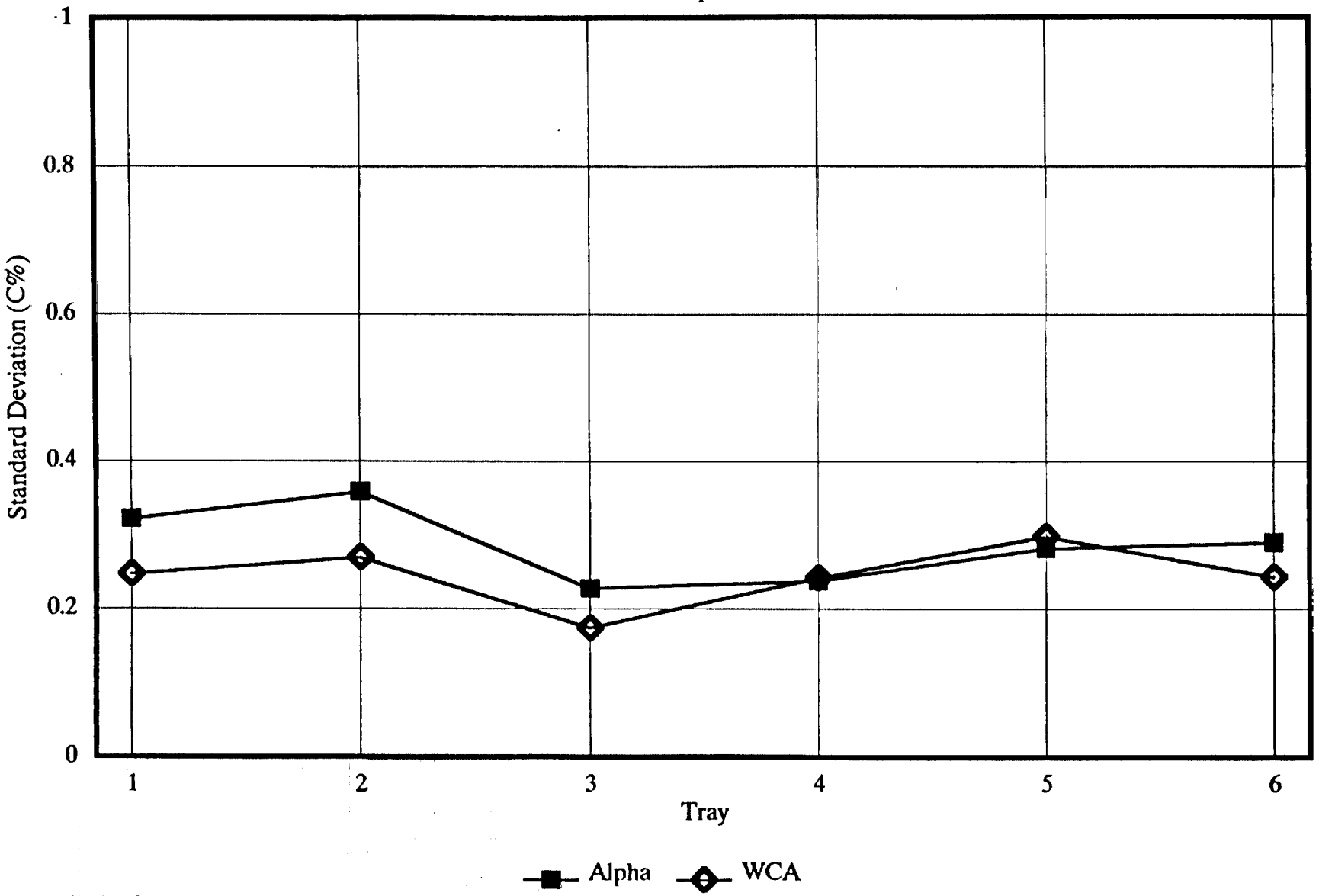


BPCHI F&M, Gardena

BPCHI F&M, Gardena

Carbon Assay Testing

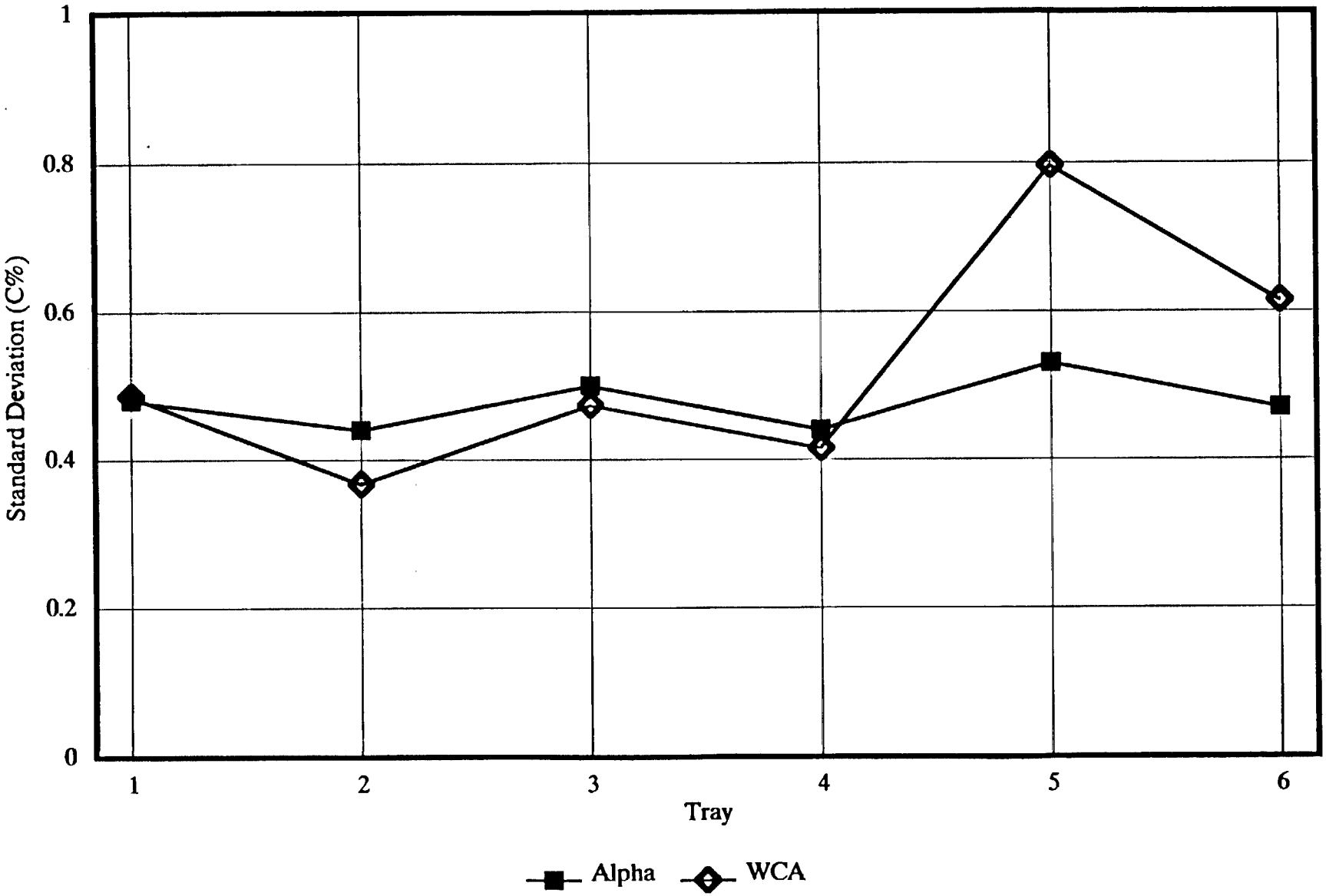
Standard Deviation Comparison – Old CHN–600



BPCHI F&M, Gardena

Carbon Assay Testing

Standard Deviation Comparison – New CHN–600



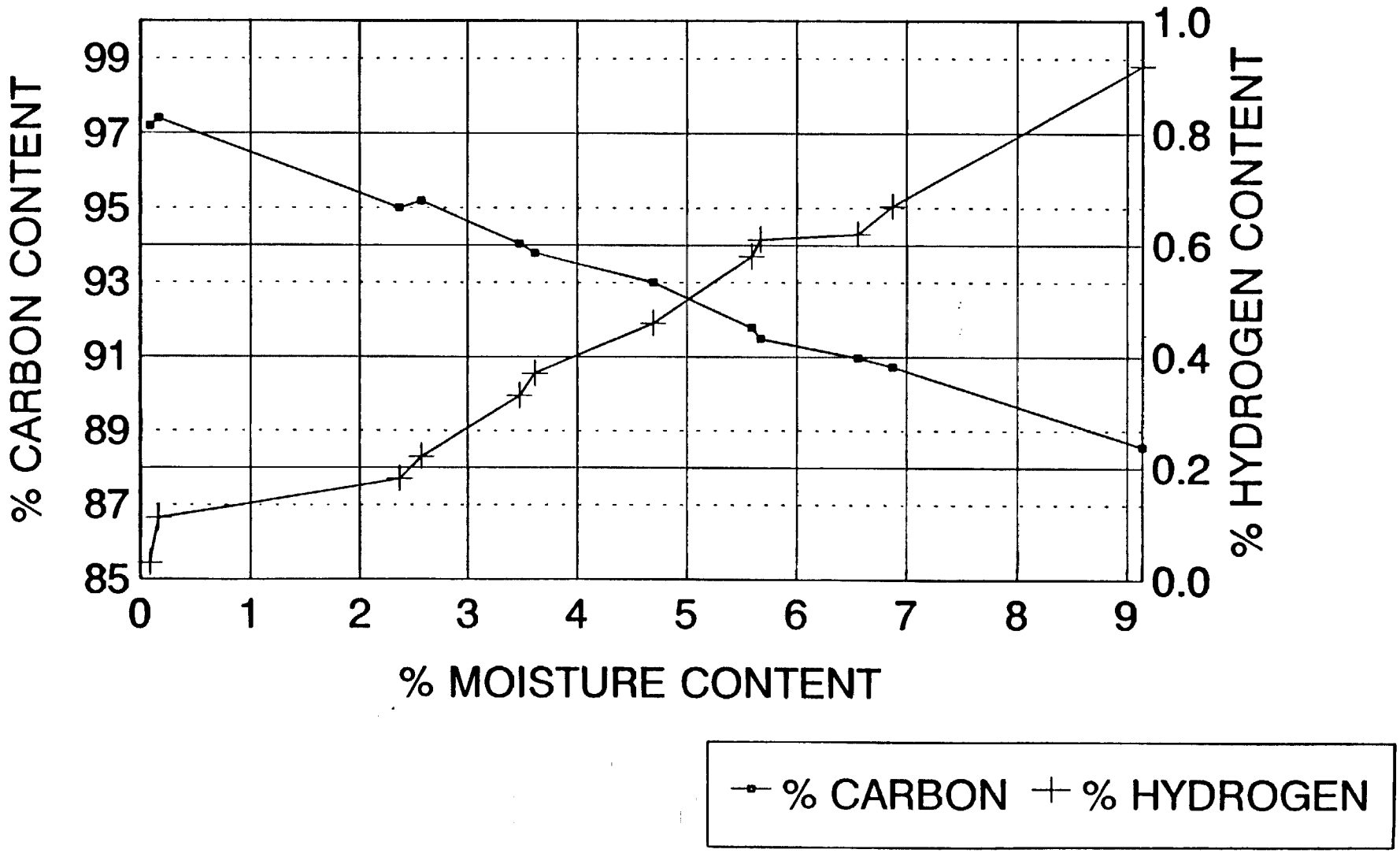
BPCHI F&M, Gardena

Carbon Assay Testing
Possible Source of Error

- Moisture - Drying, Sealing
- Performed study to confirm moisture influence
  - C%, H% vs Moisture %
  - Fabric moisture pick-up rate during testing

CARBON & HYDROGEN / MOISTURE

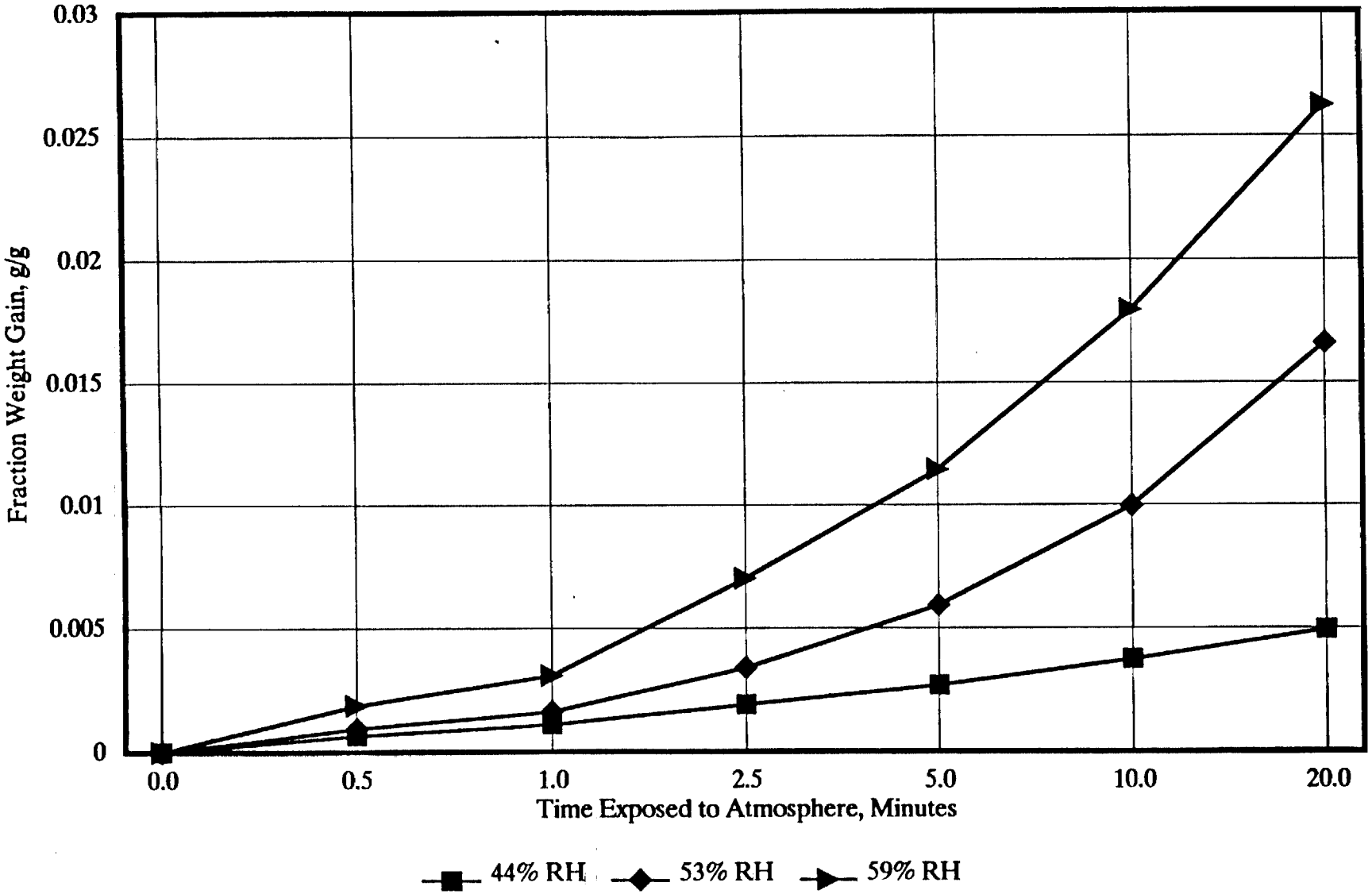
CORRELATION



BP CHEMICALS (HITCO) INC.
FIBERS & MATERIALS, GARDENA

Carbon Fabric Weight Gain

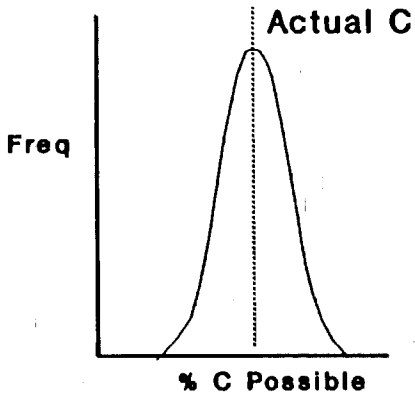
CCA8, Roll Number 25015



Dried 4 hrs @ 125C, Dessicated 2 hrs.
BPCHI F&M, Gardena

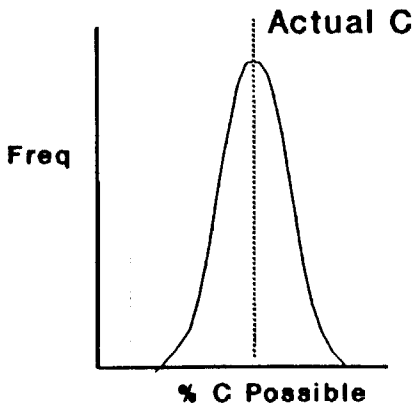
Carbon Assay Testing
System Capability

Variation during calibration



+

Variation during testing unknown sample



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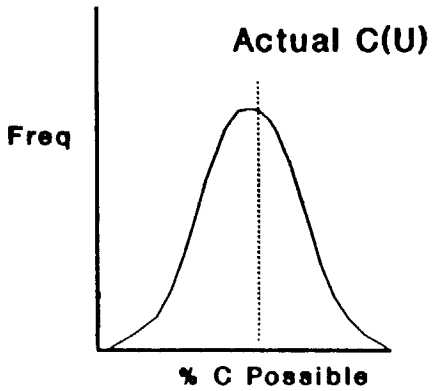
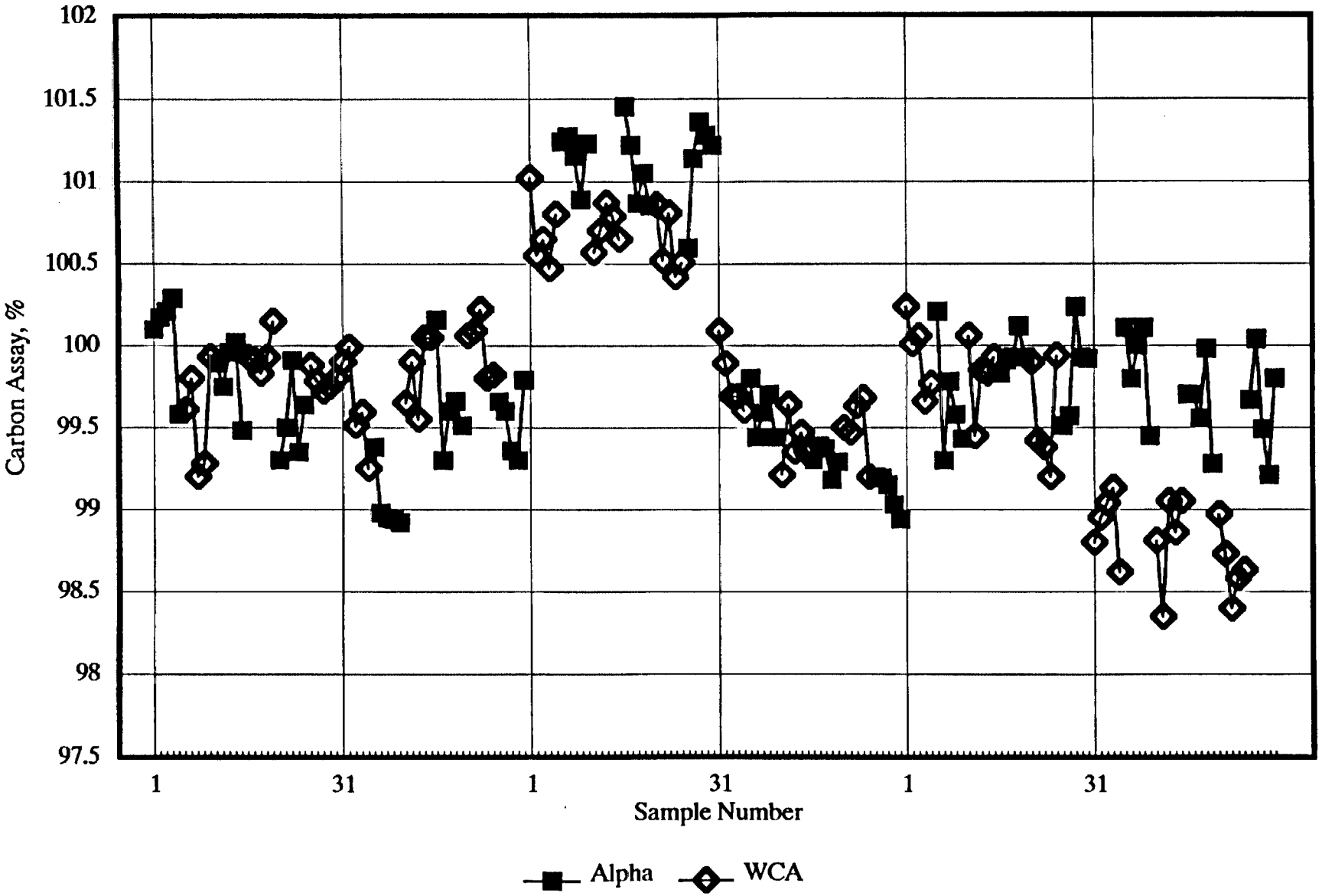
More Variation ?



BPCHI F&M, Gardena

Carbon Assay Testing

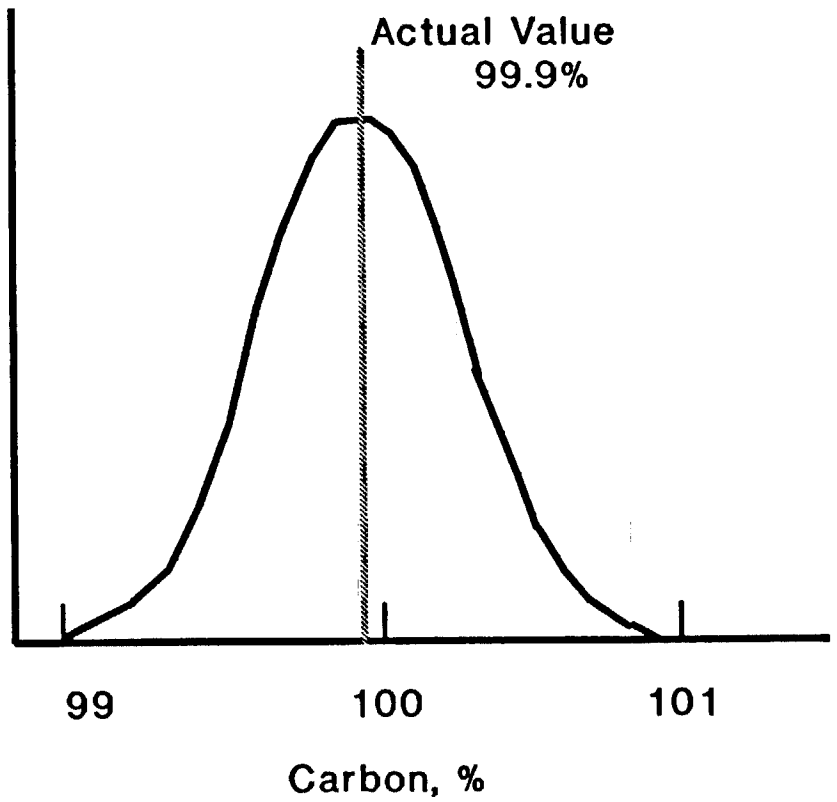
Run Chart for Old CHN-600



BPCHI F&M, Gardena

Carbon Assay Testing
System Capability

Assume



Then

50% chance that a single value will be > 100%

25% chance that two sequential values will be > 100%

12.5% chance that three sequential values will be > 100%

BPCHI F&M, Gardena

Carbon Assay Testing
Conclusions

- Standard selection
  - No clear "winner".
  - BPCHI F&M to continue with Alpha unless directed by a program.

- Machine and technician variation will be investigated.

- Moisture
  - May cause significant variation
  - Test procedure must mitigate (Drying procedure, use H%, etc)

- Capability
  - How will programs handle C% greater than 100?

BPCHI F&M, Gardena

APPENDIX M

ROMAN LOZA

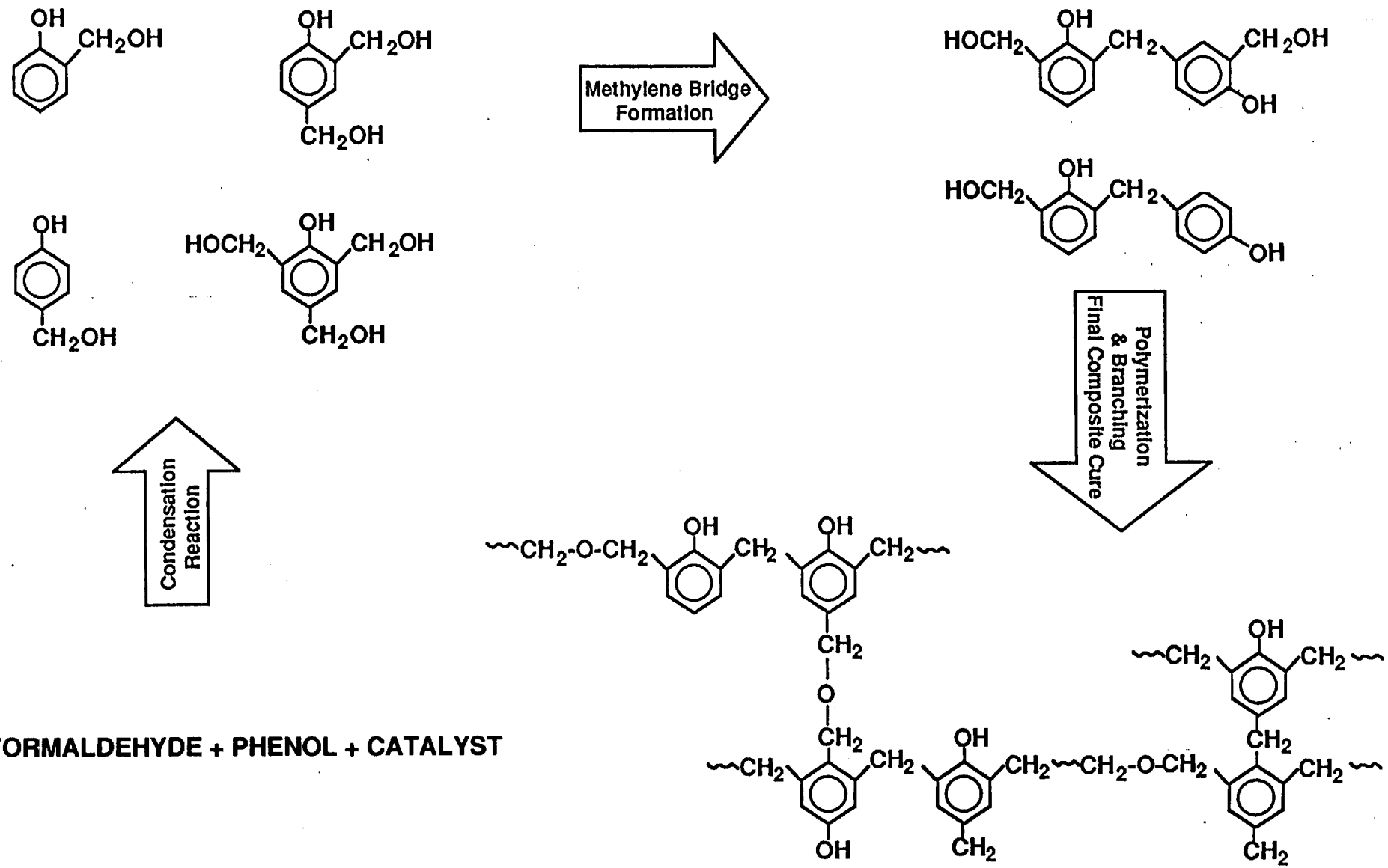
INTRODUCTION

- Develop NMR/IR spectroscopic techniques capable of quantifying the degree of advancement in phenolic resins.

- Compile NMR/IR data on phenolic resins used by F&M to establish a data base.

- Understand the chemistry of phenolic resins.

CHEMISTRY OF PHENOL FORMALDEHYDE RESINS
DIFFERENT STAGES OF CONDENSATION

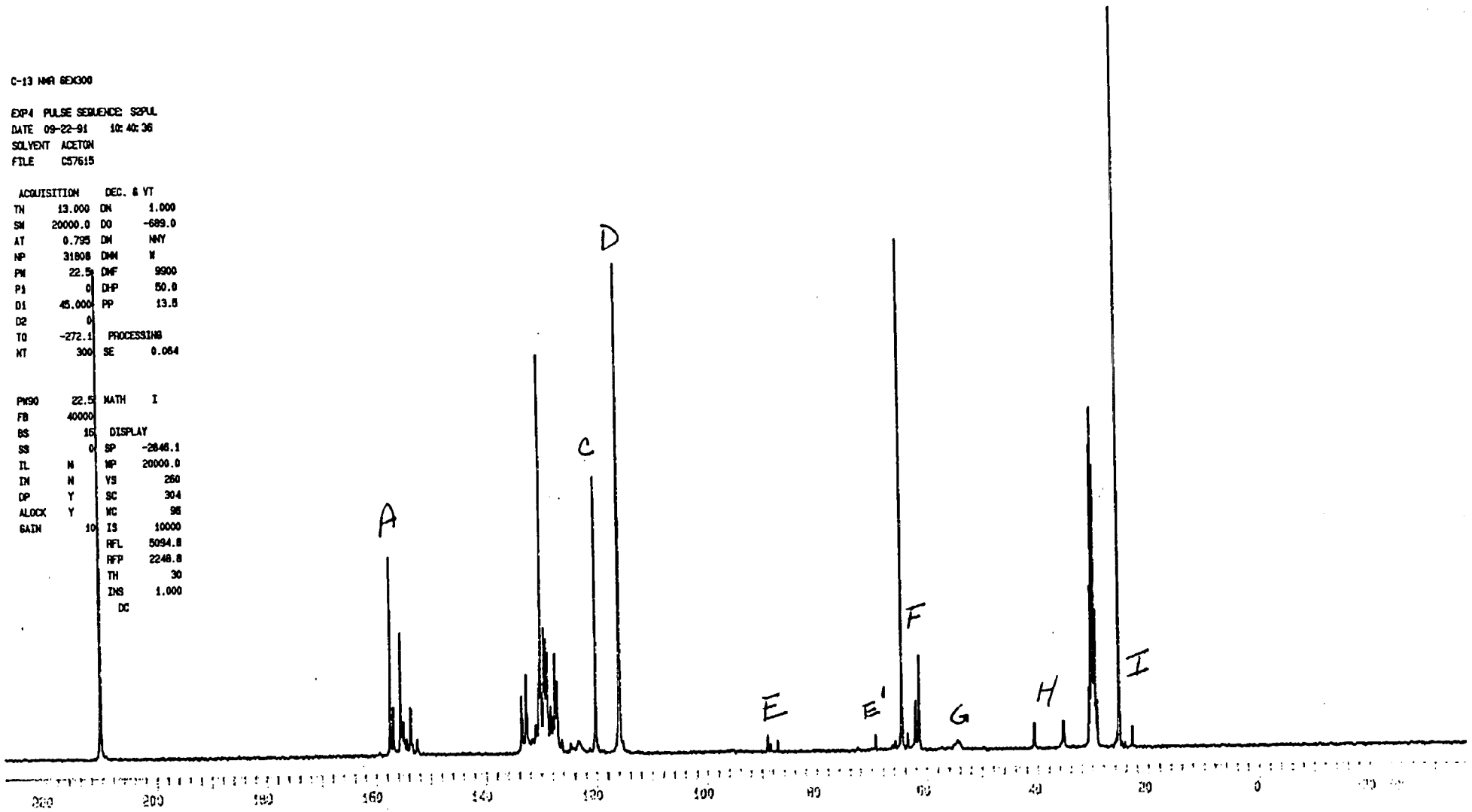


PHENOLIC RESINS

STRUCTURAL INFORMATION

C-13 Nmr Assignments

Group	Resonance (ppm)	Assignment
A	**160-152**	**Aromatic C-O (phenol carbons) including unsubstituted phenol (ca.157.7-157.3).**
B	134-126	Substituted aromatic, unsubstituted meta-aromatic.
B'	126-122	ortho-Substituted aromatic (tentative).
C	**121-119**	**para-Unsubstituted.**
D	**118-116**	**ortho-Unsubstituted.**
E	**90-86**	**-OCH_2O- (formals).**
E'	**70-65**	**$ArCH_2OR$ (R = formal).**
F	**65-60**	**Ar-CH_2OH and isopropanol (IPA).**
G	**60-52**	**Amine derivatives (tentative).**
H	**42-32**	**Ar-CH_2-Ar**
I	**26-22**	**Isopropyl methyl groups (isopropanol and isopropyl formals).**


C-13 NMR GEX300
EXP4 PULSE SEQUENCE: S2PUL
DATE 09-22-91 10:40:36
SOLVENT ACETON
FILE C57615
ACQUISITION
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SW 20000.0
AT 0.795
NP 31808
PW 22.5
P1 0
D1 45.000
D2 0
TO -272.1
NT 300
PW90 22.5
FB 40000
BS 16
SS 0
IL N
IN N
DP Y
ALOCK Y
GAIN 10
DEC. & VT
DN 1.000
DO -689.0
DM NNY
DMM M
DMF 9900
DHP 50.0
PP 13.8
PROCESSING
SE 0.064
MATH I
DISPLAY
SP -2646.1
WP 20000.0
VS 260
SC 304
WC 96
IS 10000
RFL 5094.8
RFP 2248.8
TH 30
INS 1.000
DC
A
C
D
E
E'
F
G
H
I
200
180
160
140
120
100
80
60
40
20
0

Technical Support for BPCHI
Phenolic Resin Chemistry

AGING STUDIES

Conditions: Room Temperature (21.5°C)
Time -- 1 to 90 days

Monitoring:

IR: -1024/1000 and
- 826/1000 peak ratio.

NMR: -Formaldehyde CH_2 distribution
-Phenol substitution.

Viscosity: -Brookfield viscosity.

Technical Support for BPCHI
Phenolic Resin Chemistry

AGING STUDIES

IR Results:

1024/1000 -- Decreases with time then levels off

826/1000 -- Increases with time then levels off.

Brookfield Viscosity Results:

Relative viscosity (viscosity @ time= t days/viscosity @ time=1 day) increases linearly with time.

100% increase after 22 days

Technical Support for BPCHI
Phenolic Resin Chemistry

AGING STUDIES

Nmr Results:

Formaldehyde Distribution (mole %):

$-OCH_2O-$ (Formal)	Drops to zero.
$ArCH_2OR$ (Methylol)	Increases then decreases
$ArCH_2Ar$ (Methylene bridge)	Increases linearly
$ArCH_2N-$ (Amine bridge)	No Change

% Unsubstituted Phenol (PhOH):

Decreases then no change.

Degree of ortho/para-substitution (w/o PhOH):

% Ortho-substitution	increases then no change.
% Para-substitution	increases (two rates --faster then slower).

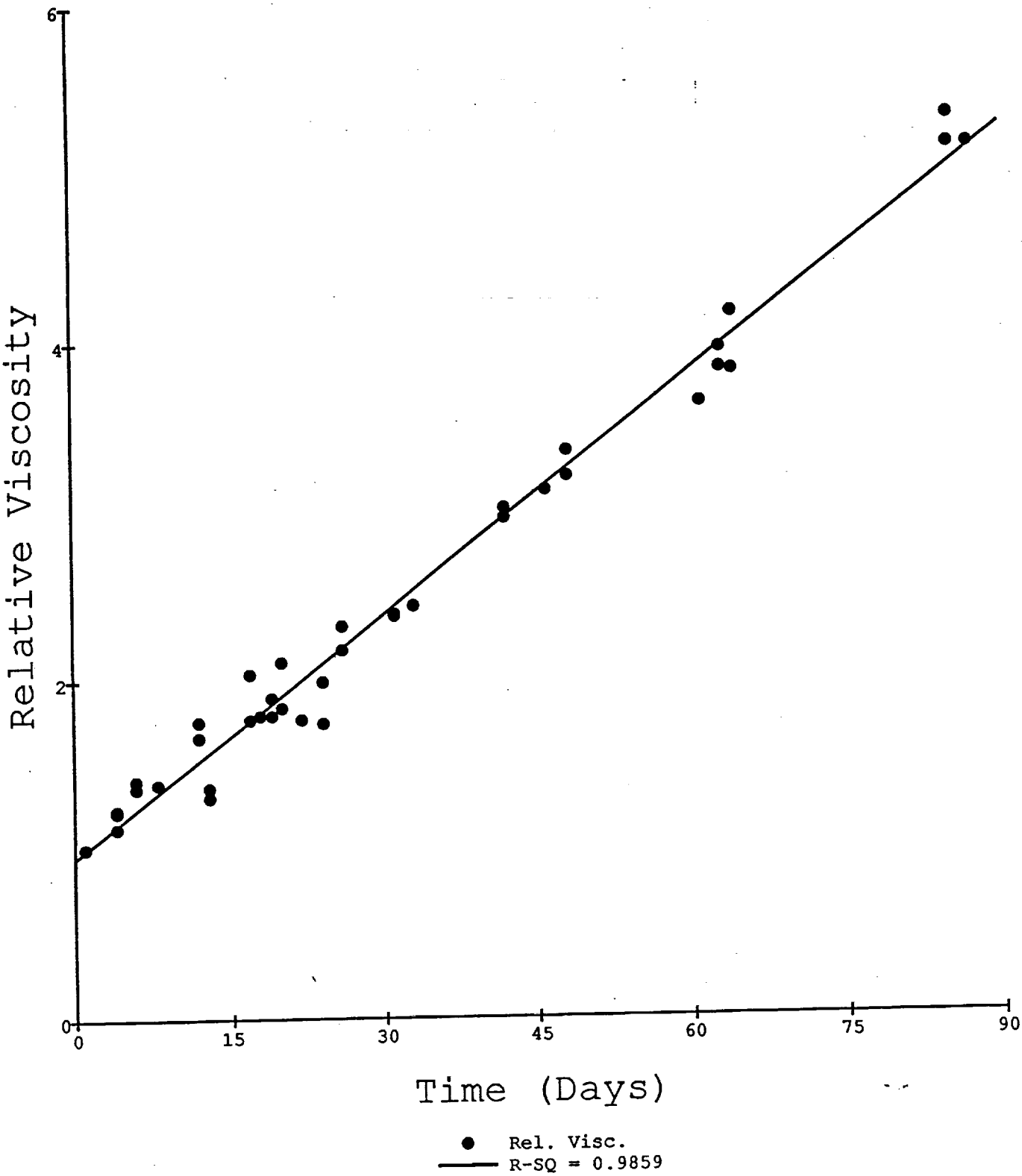
Formaldehyde (CH_2)/Total Phenolic (C-O):

No change.

IPA/Total Phenolic C-O:

No change.

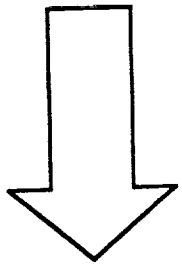
Aging Studies
Relative Viscosity vs. Time



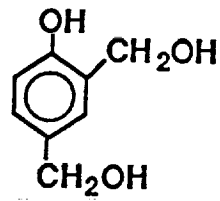
Equation of line:
Rel. Visc. = 4.78e-02*X +0.9527
Rel. Visc. = (Visc. @ time=X days)/(Visc. @ time=1 day)
Rel. Visc. data has generated from 5 different resins.

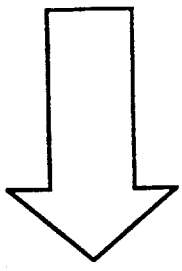
CHEMISTRY OF PHENOL FORMALDEHYDE RESINS
ROOM TEMPERATURE AGING
PROPOSED REACTION SEQUENCE

Unreacted Formaldehyde as **"Formals"** $RO-(CH_2O)_n-OH$

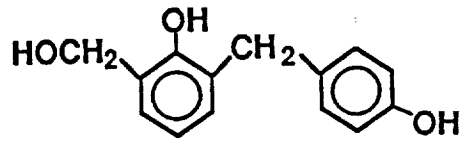


"Methylols"





"Methylene Bridged" Phenolics



APPENDIX N

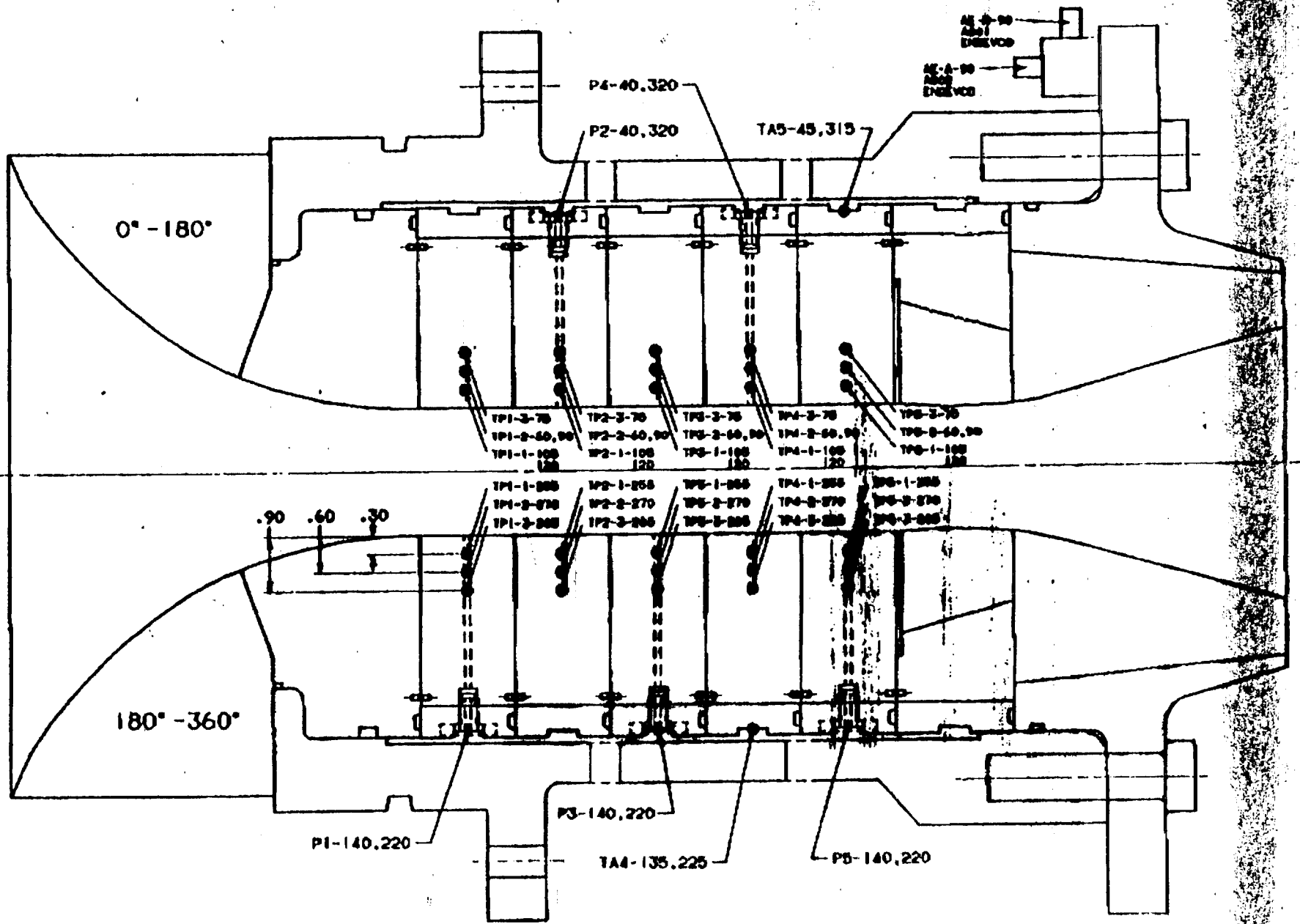
KEITH HILL

NORMALIZED EROSION & MATERIAL DESCRIPTIONS

MATERIAL	EROSION, MILS	DENSITY	RESIN	FIBER	FIRING TEMP, °C
FM 5928	287	1.62	P-39	HITEX 6K	1650
FM 5804	288	1.59	P-39	AVCARB 1200d	2300
MX 4934	290	1.52	GRF D1216	T340/3K	2300
MX 4933	300	1.69	MOD PHENOLIC	T340/3K	2300
MX 4921	312	1.54	SC1008	PANEX 1600d SPUN	1650
MX 4936	319	1.51	GRF D1216	AS4 1680d HELTRA SPUN YARN	2300
FM 5879D	315	1.63	91LD	HITEX 6K	1650
FM 5055	340	1.46	91LD	NARC RAYON	1300
MX 4904	347	1.55	SC1008	AVCARB 1600d TEXTRON SPUN	1650
MX 4902	345	1.46	SC1008	T35C/35XLD	1650
FM 5796A	346	1.62	P-39	T300/6K	1250
FM 5834B	360	1.59	91LD	HITEX 12K SPUN YARN	1650
FM 5834C	358	1.56	91LD	T300 1650d HELTRA SPUN YARN	1650
MX 4952	366	1.39	IRONSIDES FF26	T350/35XLD	1650
MX 4922	400	1.58	SC1008	AS4/6K	1250
FM 5055B	400	1.48	91LD	AVTEX RAYON	1300

NORMALIZED AFFECTED DEPTH & MATERIAL DESCRIPTIONS

MATERIAL	NORMALIZED AFFECTED DEPTH	DENSITY	RESIN	FIBER	FIRING TEMP, °C
FM 5055B	.85 - .98	1.48	91LD	AUTEX RAYON	1300
FM 5834C	1.10	1.56	91LD	T300 1680d HELTRA SPUN YARN	1650
MX 4904	1.13	1.55	SC1008	AVCARB 1600d TEXTRON SPUN YARN	1650
MX 4921	1.14	1.54	SC1008	PANEX 1600d SPUN YARN	1650
MX 4902	1.17 - 1.43	1.46	SC1008	T350/35XLD	1650
MX 4922	1.24	1.58	SC1008	AS4/6K	1250
FM 5055	1.24	1.46	91LD	NARC RAYON	1300
MX 4952	1.24	1.39	IRONSIDES FF 200	T350/35XLD	1650
FM 5928	1.24	1.62	P-39	HITEX 6K	1650
FM 5834B	1.25 - 1.37	1.59	91LD	HITEX 12K SPUN	600/1000/1650
FM 5804	1.28	1.59	P-39	AVCARB 1200d	2300
FM 5879D	1.31 - 1.36	1.63	91LD	HITEX 6K	1200/1650
FM 5796A	1.34	1.62	P-39	T300/6K	2300
MX 4933	1.75	1.63	MOD. PHENOLIC	T300/3K	2300
MX 4934	?	1.52	GRF D1216	T300/3K	2300
MX 4936	?	1.51	GRF D1216	AS4 1680d HELTRA SPUN YARN	2300


P4-40,320
P2-40,320
TA5-45,315
0° - 180°
.90
.60
.30
180° - 360°
P3-140,220
P1-140,220
TA4-135,225
P5-140,220

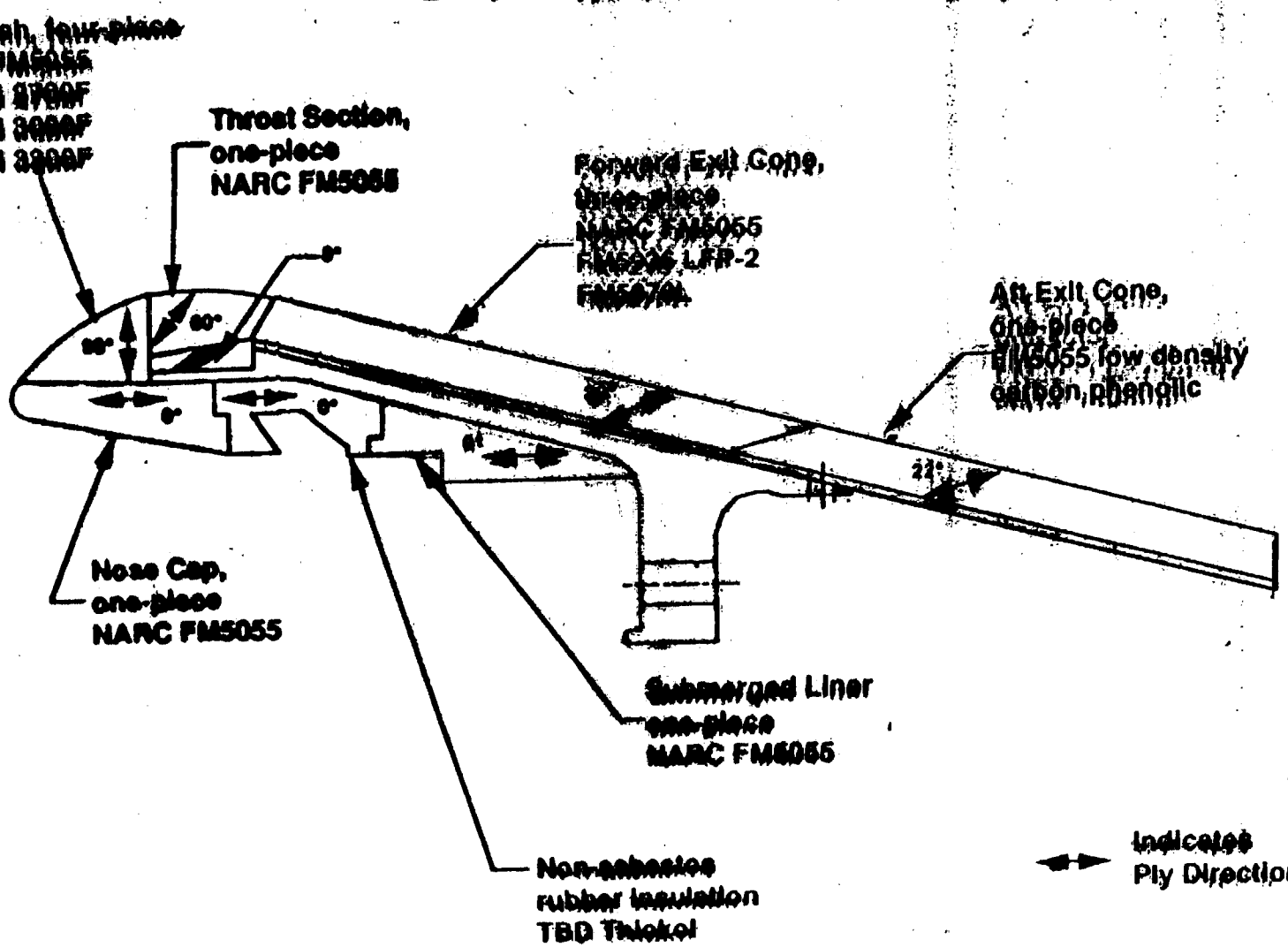
6/24/91

Standard PAN Candidate Materials for FPC's

PRODUCT	FIBER	HEAT TREAT	PAN SOURCE	WEAVE	RESIN	FILLER
Throat/Approach						
MX4933	T300/3K	2300°C	Domestic	5 HS	Modified Phenolic	Graphite
MX4934	T300/3K	2300°C	Domestic	5 HS	GRF D1216	Graphite
MX4936	AS4 1680d Hellra Spun Yarn	2300°C	Domestic	6 HS	GRF D1216	Graphite
FM5804A	Avcarb 1200 d Textron Spun Yarn	Batch Graphitized 2300°C	Foreign	5 HS	P-39	Graphite
Standard Density						
MX4904CP	Avcarb 1600d Textron Spun Yarn	1650°C	Foreign	5 HS	SC 1008	High Purity Carbon
MX4972	T350/35XLD	1650°C+	Domestic	5 HS	SC 1008	High Purity Carbon
FM5834B	Hitex HK SAW	1650°C	Foreign	(5HS)	91LD	USP 28
FM5879D	Hitex 6K	1650°C	Foreign	5 HS	91LD	USP 28
FM5928	Hitex 6K	1650°C	Foreign	5 HS	P-39	USP 28
FM5834C	T300 1680d Hellra Spun	1650°C	Domestic	5 HS	91LD	USP 28
MX4921	Panex 1600d Spun Yarn	1650°C	Foreign	5 HS	SC 1008	High Purity Carbon
FM5879L	AS4	1250°C	Domestic	5 HS	91LD	USP 28
MX4952	T350/35XLD	1650°C	DOMESTIC	5HS	FF26	USP 28
MX4963	T350/35XLD	1650°C	DOMESTIC	5HS	SC1008	USP 28

Figure 7. SPIP 48-2 Nozzle Design

SPIP 48-2 NOZZLE DESIGN



Standard PAN Candidate Materials for FPC's

PRODUCT	FIBER	HEAT TREAT	PAN SOURCE	WEAVE	RESIN	FILLER
Throat/Approach						
MX4933	T300/3K	2300°C	Domestic	5 HS	Modified Phenolic	Graphite
MX4934	T300/3K	2300°C	Domestic	5 HS	GRF D1216	Graphite
MX4936	AS4 1680d Hoitra Spun Yarn	2300°C	Domestic	6 HS	GRF D1216	Graphite
FM5804A	Avcarb 1200 d Textron Spun Yarn	Batch Graphitized 2300°C	Foreign	5 HS	P-39	Graphite
Standard Density						
MX4904CP	Avcarb 1600d Textron Spun Yarn	1650°C	Foreign	5 HS	SC 1008	High Purity Carbon
MX4972	T350/35XLD	1650°C+	Domestic	5 HS	SC 1008	High Purity Carbon
FM5834B	Hitex 6K SPUN	1650°C	Foreign	(5HS)	91LD	USP 28
FM5879D	Hitex 6K	1650°C	Foreign	5 HS	91LD	USP 28
FM5928	Hitex 6K	1650°C	Foreign	5 HS	P-39	USP 28
FM5834C	T300 1680d Hoitra Spun	1650°C	Domestic	5 HS	91LD	USP 28
MX4921	Panex 1600d Spun Yarn	1650°C	Foreign	5 HS	SC 1008	High Purity Carbon
FM5879L	AS4	1250°C	Domestic	5 HS	91LD	USP 28
MX4952	T350/35XLD	1650°C	DOMESTIC	5HS	FF26	USP 28
MX4963	T350/35XLD	1650°C	DOMESTIC	5HS	SC1008	USP 28